BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JANUARY, 1942.

I.—ALIPHATIC.

Microscopical methods for identifying organic substances. L. Kofler (*Angew. Chem.*, 1940, **53**, 167—168).—Microscopical methods are outlined for identifying substances by m.p., n (by comparison with particles of glass of known n), and temp. coeff. of n. A. LI.

Conversion of carbon monoxide with hydrogen [into hydrocarbons].—See B., 1941, II, 326.

Reactions involved in the liquid-phase alkylation of *iso*paraffins with olefines. S. H. McAllister, J. Anderson, S. A. Ballard, and W. E. Ross (*J. Org. Chem.*, 1941, **6**, 647—668).—Investigation has been made of the reaction between (:CHMe)$_2$ and *iso*-C_4H_{10}, *iso*-C_5H_{12}, *iso*-C_6H_{14}, and methyl*cyclo*hexane and between *iso*-C_4H_{10} and CH_2:CHMe, (:CHMe)$_2$, CHMe:CHEt, CMe_2:CH_2, CMe_2:CHMe, octenes from β-ethylhexanol (**I**), CH_2:CHMe trimerides (**II**), butene dimerides (**III**) and trimerides (**IV**), di*iso*amylene, and *cyclo*hexene (**V**) in presence of H_2SO_4. All the products obtained cannot be accounted for by any single reaction mechanism but the products may be broadly classified on the basis of the type of reaction which produces them. The possible reaction mechanisms are as follows. (*a*) Direct alkylation defined as the coupling of the olefine and the *iso*paraffin to form a product of the expected mol. wt.; this should not involve any structural rearrangement within the hydrocarbons themselves. However, the products obtained on alkylation with H_2SO_4 are not those expected from simple addition of the *iso*paraffin to the double linking although they may have the expected mol. wt.; with normal olefines paraffins of the expected mol. wt. constitute the principal portion of the product but this is not the case with *iso*olefines and olefine polymerides. (*b*) Hydrogenation (alkylation and de-alkylation); this reaction occurs to some extent in most alkylations and may be the main change with (**II**) and (**III**). The presence of C_3H_8 in the product from *iso*-C_4H_{10} and CH_2:CHMe and of $CHMe_2Et$ in that from CMe_2:CHMe and *iso*-C_4H_{10} is thus simply explained, as is the production of γ-methylheptane from *iso*-C_4H_{10} and (**I**). Whether or not the hydrogenation transfer actually occurs through alkylation followed by dealkylation is undecided. (*c*) Polymerisation and depolymerisation. The formation of a large proportion of octanes from *iso*-C_4H_{10} and (**IV**) is evidence that this reaction can occur in the case of highly branched olefines and this is not surprising as it is known that di- and tri-*iso*butene are depolymerised by the usual polymerisation catalysts. Hydrogenation of the trimerides is also an accompanying reaction. With the "hot acid dimerides" it is uncertain whether hydrogenation or depolymerisation predominates. (*d*) Rearrangement of primary products. There is some evidence that isomerisation or structural rearrangement may account for some of the products obtained. The production of methyl*cyclo*pentane from *iso*-C_4H_{10} and (**V**) indicates that hydrogenation and isomerisation has occurred. However, ring contraction takes place more readily than paraffin isomerisation and the experimental data tend to show that isomerisation of the primary products is at least of secondary importance. The hypothesis that the *iso*paraffin by reason of its branched structure contains labile H (whether *tert.* or present in Me) which is removed under the influence of the acid to give a radical or ion which adds to the olefine to give a saturated paraffin is inadequate unless it is assumed that isomerisation of the primary products of alkylation occurs; this seems unlikely. However, if it is assumed that the *iso*paraffin undergoes dehydrogenation then C–C cleavage is even more plausible on the basis of the bond energies involved. The energies involved in cleaving the C–H and C–C linkings are 100 and 83 kg.-cal. per mol. respectively. Thus with *iso*-C_4H_{10} the main reaction is $CHMe_3 \rightarrow \cdot CHMe_2 + Me = CHMe$:$CH_2 + CH_4$ and the secondary change is $CHMe_3 \rightarrow CMe_2$:$CH_2 + H_2$. Assuming that alkyl fragments are formed by cleavage of the *iso*paraffin during the alkylation reaction, then the addition of these fragments to the olefine double linkings gives products of the expected mol. wt. and in most cases of the structures actually obtained. H. W.

Preparation of alkyl chlorides.—See B., 1941, II, 328.

Purification of tetrachloroethylene.—See B., 1941, II, 327.

Manufacture of di-iodoacetylene.—See B., 1941, II, 328.

Purification of ether.—See B., 1941, II, 329.

Effect of hydrocyanic acid on disulphides. H. Fraenkel-Conrat (*J. Amer. Chem. Soc.*, 1941, **63**, 2533—2534).—At p_H 5 and 35° HCN converts the S_2 of cystine or glutathione into 2SH, which may explain its activating effect on papain etc. R. S. C.

Bromination of aliphatic acids and their acyl derivatives. M. S. Kharasch and L. M. Hobbs (*J. Org. Chem.*, 1941, **6**, 705—712).—Solutions of Br in the requisite acid or acyl derivatives are sealed in glass tubes after being degassed or degassed and charged with O_2 and heated in the dark or exposed to light; after suitable intervals the products are cooled in solid CO_2–$COMe_2$ and residual Br is determined. Bromination of $EtCO_2H$ and $Pr^{\alpha}CO_2H$ is accelerated by light, catalysed by O_2, and inhibited by H_2O. The rate of bromination of AcOH is little affected by light or by the presence of O_2. Light accelerates the bromination of EtCOCl and $Pr^{\alpha}COCl$ and of the corresponding anhydrides. O_2 inhibits both the dark and the illuminated reactions. The effects of light and O_2 on the bromination of AcCl and Ac_2O are much smaller than those on the reactions of the higher homologues; the dark reactions are faster than those of the higher homologues. Light and O_2 have comparatively little effect on the rate of bromination of AcBr, EtCOBr, and $Pr^{\alpha}COBr$. It appears impossible that all the reactions studied involve analogous intermediates and proceed by essentially similar mechanisms. Bromination of $EtCO_2H$ and $Pr^{\alpha}CO_2H$ (and presumably long-chain aliphatic acids) proceeds by a chain reaction involving Br atoms and is essentially similar to the bromination of PhMe, phenanthrene, and *cyclo*hexene. The bromination of AcOH has different characteristics. Since AcOH has a relatively high dielectric const. and since it appears that primary H atoms (not in close proximity to an activating group such as Ph) are not replaced by Br by an O_2-catalysed or light-accelerated reaction it is probable that AcOH does not react with Br by a Br-at. mechanism. The position with regard to acyl derivatives is more complicated. H. W.

Rates of ammonolysis of α-halogeno-acids and α-halogeno-acylpeptides.—See A., 1942, I, 25.

Mechanism of lactone hydrolysis. A. R. Olson and J. L. Hyde (*J. Amer. Chem. Soc.*, 1941, **63**, 2459—2461).—When β-butyrolactone is hydrolysed by H_2O containing $H_2{}^{18}O$ at 25° and the K salt of the resulting acid is decomposed at 200 ± 3° to CHMe:CH·CO_2K and H_2O, the distribution of ^{18}O between the products depends on the amount of excess of KOH added to the salt, thus confirming the views of Olson *et al.* (A., 1939, I, 32). R. S. C.

Action of heat on γ-alkoxybutyryl chlorides. F. F. Blicke, W. B. Wright, jun., and M. F. Zienty (*J. Amer. Chem. Soc.*, 1941, **63**, 2488—2490).—When OMe·$[CH_2]_3$·CO_2H (**I**) and

$SOCl_2$ in light petroleum are kept at room temp. for 12 hr. and the solvent and $SOCl_2$ are then removed in vac., $OMe{\cdot}[CH_2]_3{\cdot}COCl$ (**II**) is obtained. However, (**I**) and boiling $SOCl_2$ give $Cl{\cdot}[CH_2]_3{\cdot}CO_2Me$ (**III**), identified by conversion into γ-butyrolactone and $Cl{\cdot}[CH_2]_3{\cdot}CO_2H$ (anilide, *p*-toluidide, benzylamide) and by the reactions, $\rightarrow I{\cdot}[CH_2]_3{\cdot}CO_2Me \rightarrow NEt_2{\cdot}[CH_2]_3{\cdot}CO_2Me \rightarrow NEt_2{\cdot}[CH_2]_3{\cdot}CO_2H$. The conversion probably occurs thus: $2(\mathbf{II}) \rightarrow OMe{\cdot}[CH_2]_3{\cdot}CO_2Me + Cl{\cdot}[CH_2]_3{\cdot}COCl \rightarrow 2(\mathbf{III})$, although the second step could not be realised separately. Acid chlorides are similarly obtained from $OR{\cdot}[CH_2]_2{\cdot}CHEt{\cdot}CO_2H$ and $OR{\cdot}[CH_2]_2{\cdot}CH(CO_2H){\cdot}[CH_2]_2{\cdot}Ph$ (R = Me, Et, or Bu) by $SOCl_2$ at room temp. but give the γ-Cl-esters when distilled in vac. $OR{\cdot}[CH_2]_2{\cdot}CO_2H$ (R = Et or Bu) and boiling $SOCl_2$ give $Cl{\cdot}[CH_2]_3{\cdot}CO_2R$, but $OR{\cdot}[CH_2]_2{\cdot}CO_2H$ (R = Me or Et) gives only the acid chloride. *γ-Dimethylamino-*n*-butyric acid hydrochloride*, m.p. 102° (*Et* ester *hydrochloride*, m.p. 113°), and *Bu γ-chlorobutyrate*, b.p. 93—96°/8 mm., are described. R. S. C.

Production of maleic anhydride.—See B., 1941, II, 329.

Preparation of dialkyl methylenemalonates.—See B., 1941, II, 330.

Manufacture of succinic acid and esters.—See B., 1941, II, 330.

Synthesis of reductones. F. Micheel and H. Haarhoff (*Annalen*, 1940, **545**, 28—32).—The condensation (A., 1934, 1332) of 2 mols. of $OBz{\cdot}CH_2{\cdot}CO_2Et$ (**I**) to 3 : 4-dihydroxytetrone [hydroxytetronic acid] (for nomenclature cf. A., 1937, II, 441) cannot be applied to higher homologues; the C atom undergoing condensation must generally carry 2 H. *CH_2Ph iodoacetate*, b.p. 159—159·5°/12 mm. [from $CH_2Cl{\cdot}CO_2{\cdot}CH_2Ph$ (**II**) and NaI in $COMe_2$], and NaOBz in boiling $COMe_2$ give *CH_2Ph benzoyloxyacetate*, m.p. 59—60° [more conveniently obtained from (**II**), NaI, and NaOBz in $COMe_2$], which with *dl*-$OBz{\cdot}CHMe{\cdot}CO_2Et$ and K in C_6H_6 and N_2 at 90—95°, followed by EtOH, affords 30% of dl-3 : 4-*dihydroxy-5-methyltetrone*, m.p. 174°. Condensation of (**I**) with Et dibenzoyl-glycerate or -tartrate could not be effected. $CH_2I{\cdot}CO_2Ph$ and *Ph benzoyloxyacetate*, m.p. 67·5°, are prepared as for the CH_2Ph esters. H. B.

Metabolism of *l*- and *dl*-α-hydroxy-β-benzylthiolpropionic acid and *dl*-α-hydroxy-γ-benzylthiolbutyric acid in rats. J. A. Stekol (*J. Biol. Chem.*, 1941, **140**, 827—831).—*S*-Benzyl-*l*-cysteine with $Ba(NO_2)_2$–H_2SO_4 yields *l*-α-*hydroxy-β-benzylthiolpropionic acid*, $[\alpha]_D^{23}$ − 56·2° in 95% EtOH; similarly, *dl*-*S*-benzylcysteine gives the *dl*-acid, whilst *S*-benzyl-*dl*-homocysteine (du Vigneaud and Patterson, A., 1935, 737) affords dl-α-*hydroxy-γ-benzylthiolbutyric acid*. Methionine treated with Na in liquid NH_3 forms homocysteine; with excess of Na and CH_2PhCl NNS-*tribenzyl*-dl-*homocysteine*, m.p. 180—185° (decomp.), is formed. (See also A., 1942, III, 46.) R. L. E.

Manufacture of formaldehyde.—See B., 1941, II, 330.

Thermal decomposition of acetaldehyde. J. C. Morris (*J. Amer. Chem. Soc.*, 1941, **63**, 2535—2536).—The arguments of Burton *et al.* (A., 1940, II, 154) are inconclusive. No exchange of H and D occurs in the methanes evolved by decomp. of mixed MeCHO-$CD_3{\cdot}CDO$ at 535°; the decomp. is thus 80—100% mol. and not a chain reaction. R. S. C.

Reduction of methyl *n*-propyl ketone to pentane at cadmium–bismuth cathodes.—See A., 1942, I, 25.

Production of unsaturated amines.—See B., 1941, II, 330.

Action of sodium on ββ′-dichlorodiethylamine. P. A. Lasselle and S. A. Sundet (*J. Amer. Chem. Soc.*, 1941, **63**, 2374—2376).—$(Cl{\cdot}[CH_2]_2)_2NH$ and Na in PhMe give ~35% of ? 1-vinylethyleneimine, b.p. 46·7—48·7°/690 mm., hydrogenated (Raney Ni; room temp./50 lb.; *cyclo*hexane) to 1-ethylethyleneimine (**I**), b.p. 48·5—49°/690 mm. (picrate, m.p. 111°; aurichloride, decomp. 104°). Evaporation of (**I**) with an excess of conc. HCl gives $NHEt{\cdot}[CH_2]_2{\cdot}Cl$ (*hydrochloride*, m.p. 223°; *aurichloride*, m.p. 131·5°), obtained also from $NHEt{\cdot}[CH_2]_2{\cdot}OH$ by $SOCl_2$–$CHCl_3$ and reconverted into (**I**) by 40% aq. NaOH. R. S. C.

α-Methylallylamine. J. Klueger and M. Schwarcz (*J. Amer. Chem. Soc.*, 1941, **63**, 2512—2513).—Charon's crotylthiocarbimide (A., 1899, i, 848; cf. Mumm *et al.*, *Ber.*, 1940, **73**, [*B*], 843) has b.p. 160—170° and gives a thiocarbamide (**I**), m.p. 106°, with a small amount of a compound, m.p. 60°. In boiling, conc. HCl it yields as sole pure product α-methylallylamine [γ-amino-Δ^{α}-butene], b.p. 62·3° (*picrate*, m.p. 156·5—158°), which in presence of PtO_2 in EtOH absorbs 2 H to give $CHMeEt{\cdot}NH_2$ and with CS_2–Et_2O gives a dithiocarbamate, m.p. 106°, converted by aq. $HgCl_2$ and later NH_3–EtOH–H_2O into (**I**). R. S. C.

Hydrazine series. I. Preparation of tri- and tetra-alkylhydrazines. F. Klages, G. Nober, F. Kircher, and M. Bock. **II. Thermal decomposition of quaternary hydrazonium bases.** F. Klages and G. Nober [with R. Frank] (*Annalen*, 1941, **547**, 1—38, 39—64).—I. Me_2 ketazine (Curtius *et al.*, A., 1891, 1355) and MgMeBr–Et_2O afford $NHBu^{\gamma}{\cdot}NH_2$, b.p. 129—134° (*hydrochloride*, m.p. 191—192°), hydrogenated (H_2–Ni) at 170° to NH_2Bu^{γ}, b.p. 42—43° [hydrochloride, m.p. 291° (decomp.)]. $NHBu^{\gamma}Cl$–MgBu$^{\gamma}$Cl or NBu^{γ}_2Cl–Cu-bronze yield *di*tert.-*butylamine*, b.p. 92—95° (*picrate*, m.p. 152—153°). MeCHO or CH_2O and $NMe_2{\cdot}NH_2$ give $NMe_2{\cdot}N{:}CHMe$, b.p. 89—94°, or $NMe_2{\cdot}N{:}CH_2$ (**I**), b.p. 69—73°, respectively. (**I**) and MgMeBr in PhOMe (in N_2) at 100° (bath) yield *N-dimethyl-N′-ethylhydrazine*, b.p. 76—77°/720 mm. (purified through the semicarbazide, m.p. 105—106°; *phenylsemicarbazide*, m.p. 88°; *picrate*, m.p. 92—93°). $NMe_2{\cdot}NH_2$–EtO·NO_2 at 100° 100° (bath) afford NMe_2Et, b.p. 34—35° (picrate, m.p. 202—203°). Hydrazomethane (**II**) and MgMeBr–Et_2O, then MeI at 100° (bath), give $NMe_2{\cdot}NHMe$ (purified through the picrate). N_2H_4 and $Pr^{\beta}Br$–$Pr^{\beta}OH$ at 100° (bath) yield a product, further treated by N_2H_4–$Pr^{\beta}Br$ at 110° to give mono-, b.p. 90—110°, di-, b.p. 128—139° ($(NH_2{\cdot}NPr^{\beta}_2)$ (*phenylthiosemicarbazide*, m.p. 102—103°), and *tri*iso*propylhydrazine* (**III**), b.p. 155—160° (*picrate*, m.p. 95—96°). Attempted further alkylation of (**III**) gives mixtures containing higher alkylated compounds (not purified). (**II**) and $Pr^{\beta}Br$ at 100° (bath) yield iso*propylhydrazomethane* (**IV**), b.p. 95—97° (*picrate*, m.p. 143°), whereas prolonged *iso*propylation affords *di*iso*propylhydrazomethane* (**V**), b.p. 143—145° (*picrate*, m.p. 139—140°), (**IV**), and some $NMePr^{\beta}_2$, b.p. 109—112° (*picrate*, m.p. 202—203°), also obtained from $NHMe$–$Pr^{\beta}Br$–EtOH.

II. Thermal decomp. (particularly at 110—120°, then at 150—170°, and >180°) of $[NMe_3{\cdot}NH_2]^+OH^-,1{\cdot}5H_2O$ (from the iodide and Ag_2O) yields H_2O, MeOH, NMe_3, $NHMe_2$, $CH_2(NMe_2)_2$, $NMe_2{\cdot}NH_2$, and NH_3. $[NHMe_2{\cdot}NHEt]^+OH^-$ affords $NMe_2{\cdot}NH_2 + C_2H_4$. (**V**) and MeI at 100° (sealed tube; 20 hr.) afford a mixture containing quaternary salt, which when treated with TlOH and distilled in high vac. gives NMe_2Pr^{β}, $NHMe_2$, and $NHMePr^{\beta}$; thermal decomp. of the residue of quaternary base affords NMe_3 (95%) + NMe_2Pr^{β} (5%). $[NMe_3{\cdot}NHMe]^+OH^-$, prepared from the iodide and Tl_2SO_4, yields $NHMe_2$, NH_2Me, NMe_3, and NH_3. Mechanisms of reaction are discussed. A. T. P.

α-Aminovinyl ether. F. Klages and E. Drerup (*Annalen*, 1941, **547**, 65—72).—$[CH_2{:}CBr{\cdot}NMe_3]^+Br^-$ (**I**), new m.p. 152—153° (unchanged on refluxing with aq. H_2SO_4), and NaOMe–MeOH or NaOEt–EtOH give *α-methoxy-*, m.p. 178°, or *α-ethoxy-vinyltrimethylammonium bromide*, m.p. 150—151°, respectively, hydrolysed by aq. H_2SO_4 to EtOH, AcOH, and NMe_3. (**I**) and aq. NaOH (reflux) give NMe_3 + AcOH. A. T. P.

Formation of α-aminobutyric acid on warming *l*-glutamic acid with sodium hydroxide. E. Abderhalden and O. Böhm (*Z. physiol. Chem.*, 1940, **266**, 41—42).—*l*-Glutamic acid, boiled with 20% aq. NaOH, loses CO_2 and forms *dl*-α-aminobutyric acid. J. H. B.

Relative stability of *l*(+)-lysine in rats studied with deuterium and heavy nitrogen. N. Weissman and R. Schoenheimer (*J. Biol. Chem.*, 1941, **140**, 779—795).—The introduction of D directly united to C into lysine by the Pt-catalysed exchange reaction at elevated temp. does not appear possible. *cyclo*Hexanone readily exchanges H for D when heated with D_2O in presence of active Pt but the yield is small and much C_6H_6 and *cyclo*hexanol are produced. PhOH is treated with H_2–O_2 (1 : 1) at 95°/atm. pressure, yielding a deutero*cyclo*hexanone, converted through its oxime into ε-benzamidodeuterohexoic acid. This is brominated and then converted into its Et ester, which is condensed with $C_6H_4(CO)_2NH$ containing ^{15}N at 150° in presence of CuO; the product is hydrolysed to a lysine dihydrochloride containing 7·0 at.-% D and 2·2 at.-% ^{15}N excess. This is resolved with good yields with the aid of *l*- and *d*-camphoric acid. *Et* α-*bromo*-ε-*benzamidohexoate*, m.p. 57—57·5° (corr.), is incidentally reported. (See also A., 1942, III, 42.) H. W.

N-**Methanesulphonyl derivatives of amino-acids and oligopeptides.** B. Helferich and H. Grünert (*Annalen*, 1940, **545**, 178—196; cf. A., 1938, II, 351).—Interaction of $MeSO_2Cl$, sometimes in Et_2O, with a feebly alkaline aq. solution of the requisite NH_2-acid gives methylsulphonamidoacetic acid (normal *Na* salt, m.p. 229—230°; also $+3H_2O$), *methanesulphonyl*-l-*leucine*, m.p. (anhyd.) 73°, ($+1H_2O$) ~53°, $[\alpha]_D^{20}$ −19·2° in N-NaOH, -dl-*leucine*, m.p. 109—110° (also $+1H_2O$), -dl-*phenylalanine*, m.p. 104°, and -*sarcosine*, m.p. (anhyd.) 67° (corr.), $+0{\cdot}5H_2O$, m.p. 48—48·5° (corr.). Tyrosine yields ON-*dimethylsulphonyltyrosine*, m.p. 165—166° (corr.), $[\alpha]_D^{20}$ +5·4° in N-NaOH, −13·7° in abs. EtOH, in which one acyl group is attached to the phenolic O since it is readily lost under the influence of alkali with the formation of N-*methanesulphonyl*-l-*tyrosine*, m.p. 153—154° (corr.) after softening above 147°, $[\alpha]_D^{20}$ +10·1° in N-NaOH, −11·7° in abs. EtOH. The mono-derivatives are monobasic acids which can be sharply titrated with phenolphthalein as indicator. They are freely sol. in hot, sparingly sol. in cold, H_2O. Their power of crystallising varies but is usually not very pronounced. It has not yet been possible to prepare cryst. derivatives of *l*-histidine, *l*-proline, or *l*-glutamic acid. Hot conc. NaOH or HCl hydrolyses them with great difficulty or not at all. Attempts to improve the yields of the mono-derivative (I) by use of larger proportions of $MeSO_2Cl$ and NaOH gives *NN*-dimethanesulphonyl compounds, also obtainable by further treatment of (I). *Dimethylsulphonylglycine*, m.p. 185° (corr.) [converted by $SOCl_2$ at 70° into *dimethanesulphonimidoacetyl chloride*, m.p. 124·5—125·5° (corr.)], and *dimethylsulphonyl*-dl-*alanine* (II), m.p. 200·5° (corr.), are described. Both substances are very stable to acid but are rapidly altered by alkali particularly in warm solution. Exactly 1 equiv. of acid is lost but the course of the reaction is not simple. The formation of (II) is accompanied by that of a considerable proportion of *dimethanesulphonimide* (also $+1H_2O$), m.p. 154·5—155·5° (corr.), which is remarkably stable to hot acid and alkali and can be titrated accurately as a monobasic acid in presence of phenolphthalein. It is the only product obtained in an attempt to prepare dimethanesulphonyl-*dl*-leucine. It is converted by $CHN_2{\cdot}CO_2Et$ into *Et dimethanesulphonimidoacetate*, m.p. 107·5—108·5° (corr.). Application of the method to readily available oligopeptides leads to the isolation of *methanesulphonyl-glycylglycine*, m.p. 130°, and its *Et* ester, m.p. 106°, *-sarcosylsarcosine*, m.p. 145° (corr.), *dimethanesulphonyl-glycylglycine*, m.p. 248—250° (corr.; decomp.), *-glycyl*-l-*leucine*, m.p. 171° (corr.), $[\alpha]_D^{20}$ −10·3° in N-NaOH, *-diglycylglycine*, m.p. 233·5—234° (corr.; decomp.), and *-triglycylglycine*, m.p. 173° (corr.). In these compounds $MeSO_2$ of the mono- and $(MeSO_2)_2$ of the di-derivatives is attached to the N of the terminal NH_2. This is shown by the results of hydrolysis and by the observation that ≯ 2 $MeSO_2$ groups can be introduced into a tri- or tetra-peptide by the use of an excess of the reagents. It appears that NH of a peptide linking is unable to react with $MeSO_2Cl$. Monomethanesulphonyloligopeptides are hydrolysed at the peptide linking and the terminal NH_2-acid can be isolated as its $MeSO_2$ derivative. *NN*-Dimethylsulphonyloligopeptides are hydrolysed by acids at the peptide linking and the terminal NH_2-acid can be isolated as its $(MeSO_2)_2$ derivative with particular readiness on account of the sparing solubility in H_2O. The action of alkali occurs in several directions and the isolation of individual products is difficult. H. W.

Sodium and barium salts of *N*-(**αγ-dihydroxy-ββ-dimethylbutyryl**)**taurine.**—See A., 1942, III, 61.

Addition reaction of alkali-treated silk, involving a synthesis of cystine. B. H. Nicolet and L. A. Shinn (*J. Amer. Chem. Soc.*, 1941, **63**, 2284—2285).—Treatment of whole silk with $CH_2Ph{\cdot}SNa$ in boiling ~0·1N-NaOH and reduction of the product by Na–NH_3 gives 3·3% of cysteine (I), whereas only 0·4% is obtained from untreated silk. This is due to dehydration of combined serine by alkali to a dehydroalanine peptide, addition of $CH_2Ph{\cdot}SNa$ to give *S*-benzylcystcine units, and final reduction thereof to (I). The (I) content of casein is similarly increased by 1% by incubation for 14 days in 2% aq. Na_2S. R. S. C.

Methionine and its derivatives. II. Separation of methionine from crude leucine. Y. Takayama and Y. Tsuchiya (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 503—511; cf. A., 1941, II, 316).—The crude leucine is dissolved in hot conc. HCl and the bulk of the leucine hydrochloride is removed by fractional crystallisation. The crude methionine (I) present to the extent of 40—50% in the final conc. mother-liquor is liberated by neutralisation. Pure (I) is obtained either by pptn. of the double $HgCl_2$ salt or by fractional distillation of the Et esters of (I) and leucine. The former has the higher b.p. (123—126°/15 mm.) and is hydrolysed by H_2O at 100°. J. N. A.

Manufacture of nitriles.—See B., 1941, II, 331.

Manufacture of dinitriles.—See B., 1941, 331.

II.—SUGARS AND GLUCOSIDES.

Action of hydrogen chloride in glucose. Synthesis of polyglucosan. H. H. Schlubach and E. Lührs (*Annalen*, 1941, **547**, 73—85; cf. A., 1932, 502).—Glucose saturated with HCl under pressure at room temp. to 30°, then heated at 40°/15 mm. for 5 hr., affords a product, which after acetylation (Ac_2O–C_5H_5N) and deacetylation affords a polyglucosan (I) (60%) $(C_6H_{10}O_5)_n$ (n = ? 12), $[\alpha]_D^{20}$ +124·1° in H_2O, a trisaccharide (II) (30%), $[\alpha]_D^{20}$ +99·4° in H_2O [acetate, m.p. 126—127° (sinters at 112°), $[\alpha]_D^{20}$ +94° in $CHCl_3$], and unchanged glucose (10%). (I) and Me_2SO_4–aq. NaOH–$COMe_2$ yield a compound, m.p. >100° (not sharp), $[\alpha]_D^{20}$ +125·8° in $CHCl_3$, converted by HCl–MeOH into a 1 : 2 : 1 mixture of tri-, tetra- (2 : 3 : 4 : 6), and penta-methylglucose. (II) and Ag_2O–MeI yield a derivative, $[\alpha]_D^{20}$ +106·9° in $CHCl_3$, hydrolysed to tri-, $[\alpha]_D^{20}$ +67·2° in $CHCl_3$, and 2 : 3 : 4 : 6-tetramethylglucose (1 : 2). A. T. P.

Rates of reaction of di*iso***propylidene-glucose, -galactose, and -sorbose with triphenylmethyl chloride in pyridine.** R. C. Hockett, H. G. Fletcher, jun., and J. B. Ames (*J. Amer. Chem. Soc.*, 1941, **63**, 2516—2519).—CPh_3Cl reacts with *sec.*-OH of carbohydrates, but much more slowly than with primary OH. The following are prepared. 1 : 2-5 : 6-Di-*iso*propylidene-*D*-glucofuranose, m.p. 110—111°, $[\alpha]_D^{21}$ −16·9° in H_2O [*CPh*$_3$ *ether*, m.p. 115° (corr.), $[\alpha]_D^{21\cdot5}$ −24·1° in $CHCl_3$]. 1 : 2-3 : 4-Di*iso*propylidene-*D*-galactopyranose, $[\alpha]_D^{21}$ −68·64° in C_5H_5N (prep. from the 6-acetate, m.p. 109—110°, $[\alpha]_D^{20}$ −47·2° in $CHCl_3$, by 0·2N-NaOMe–MeOH; 6-*CPh*$_3$ *ether*, m.p. 80—82°, $[\alpha]_D^{20}$ −58·4° in $CHCl_3$). 2 : 3-4 : 6-Di*iso*propylidene-*L*-sorbofuranose, m.p. 77°, $[\alpha]_D^{21}$ −16·7° in $COMe_2$ [1-CPh_3 ether, m.p. 182° (corr.), $[\alpha]_D^{21\cdot5}$ −27·5° in $CHCl_3$, −29·4° in C_5H_5N]. R. S. C.

Isolation of adenine-deoxyriboside from thymus-nucleic acid.—See A., 1941, III, 1022.

Constitution of butrin. P. S. Rao and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, **14**, **A**, 29—34).—Butrin (I), m.p. 193—194° (decomp.), in 80% MeOH is converted by a large excess of CH_2N_2 in Et_2O into 4′-O-*methylbutrin* (II), m.p. 230—232°, which is insol. in cold aq. alkali, does not give a colour with $FeCl_3$, but develops the pink colour characteristic of flavanones when reduced with Mg powder and HCl. (II) is hydrolysed by boiling 7% H_2SO_4 to a mixture of 4′-O-*methylbutrin* (III), m.p. 204—206°, which does not give a colour with $FeCl_3$ in EtOH but becomes pink when treated with Mg and HCl, and 4′-O-*methylbutein* (IV), m.p. 206—208°, which gives an olive-brown colour with $FeCl_3$ in aq. EtOH but no pink colour with Mg and HCl. The mixture is degraded by boiling 50% KOH to *iso*vanillic acid, m.p. 253—155°. (IV) is obtained synthetically from *iso*vanillin, resacetophenone, and 50% KOH in EtOH at room temp. and is slowly converted by conc. H_2SO_4 in boiling 50% EtOH into (III). It is therefore concluded that (I) is the 3′ : 7-diglucoside of butin and thus it affords the first instance of a glycoside containing the sugar residues in two different positions among the group of anthoxanthins and also the first instance of the presence of the sugar group in the side Ph nucleus among anthoxanthin and anthocyanin pigments. H. W.

Constitution of amylopectin. K. H. Meyer (*Naturwiss.*, 1940, **28**, 722; cf. A., 1940, II, 337; 1941, II, 87).—The literature on the constitution of the amylopectin mol. is reviewed. It is possible that part of the mol. remains in the lattice form of micelles, and another part of the same mol. is surrounded with solvent; on comparison, the amylose mol. is either completely dissolved, or is bound in the lattice structure with other mols. and is thus not available for " paste formation." A. T. P.

Position of branching of the starch chain. K. Freudenberg and H. Boppel (*Naturwiss.*, 1940, **28**, 264).—Hydrolysis of

completely methylated potato starch gives much 2 : 3 : 6-tri-, a little di- (I), and somewhat less 2 : 3 : 4 : 6-tetra-methylglucose. (I) is a mixture of at least 2 : 6- (produced from trimethylglucose by hydrolysis and subsequent glucosidation) and 2 : 3-dimethylglucose which arises directly from the methylated starch. It follows that the branching of the starch chain occurs at $(OH)_{(6)}$. A. J. M.

Structure of starch grain.—See A., 1941, III, 1085.

Resistance of starch from different sorts of wheat to the hydrolysing action of amylase.—See A., 1941, III, 943.

Significance of *X*-ray diffraction patterns obtained from starch granules.—See A., 1941, I, 452.

Micellular structure of cellulose and its derivatives.—See A., 1941, I, 451.

III.—HOMOCYCLIC.

Synthesis of benzene hydrocarbons from methane.—See B., 1941, II, 325.

Stabilisation of styrene.—See B., 1941, II, 332.

Polycyclic aromatic hydrocarbons. XXVIII. Dibenzfluorenes. R. H. Martin (*J.C.S.*, 1941, 679—685).—The carcinogenic hydrocarbon, 1 : 2 : 7 : 8-dibenzfluorene (I), obtained by dehydration (HPO_3) of $(1\text{-}C_{10}H_7)_2CH\cdot OH$, is oxidised ($SeO_2$) to the -fluorenone (II), which when fused with KOH gives 2 : 2′-*dinaphthyl*-1-*carboxylic acid*, m.p. 177—179°, decarboxylated (Cu) to $(2\text{-}C_{10}H_7)_2$. 3 : 2-$C_{10}H_6Br\cdot CO_2H$ is converted (Cu) through its Me ester into *Me* 2 : 2′-*dinaphthyl*-3 : 3′-*dicarboxylate*, m.p. 173—173·5°, from which by pyrolysis of the Pb salt of the *acid*, m.p. 298—299°, is obtained 2 : 3 : 6 : 7-*dibenz-fluorenone* (III), m.p. 269—270°, reduced (N_2H_4,H_2O) to the -*fluorene*, m.p. 282·5—283·5°. Fusion (KOH) of (III) yields 2 : 2′-*dinaphthyl*-3-*carboxylic acid*, m.p. 189—191°, dehydrated (80% H_2SO_4) to 1 : 2 : 6 : 7-*dibenzfluorenone*, m.p. 211°. 1 : 2-$C_{10}H_6Br\cdot CO_2Me$ and Cu give *Me* 1 : 1′-*dinaphthyl*-2 : 2′-*dicarboxylate*, m.p. 156·5—157·5°, which is converted into 3 : 4 : 5 : 6-*dibenz-fluorenone* (IV), m.p. 222—222·5° (*oxime*, m.p. 253—254°), reduced (N_2H_4,H_2O) to the -*fluorene*, m.p. 152—152·5° (*dipicrate*, m.p. 154—155°). Fusion (KOH) of (IV) affords 1 : 1′-*dinaphthyl*-2-*carboxylic acid*, m.p. 199—200°, and fusion with $AlCl_3$–NaCl yields 1 : 2 : 8 : 9-*dibenzanthrone*, m.p. 185—186°. Neither (III) nor (IV) is identical with (II) and this confirms the structure of (I). 1-$C_{10}H_7\cdot COCl$, tetrahydronaphthalene, and CS_2 with $AlCl_3$ give 1-$C_{10}H_7$ 6′-1 : 2 : 3 : 4-tetrahydronaphthyl ketone (*oxime*, m.p. 172—172·5°), dehydrogenated (Se at 220°) to 1 : 2′-dinaphthoyl ketone, reduced to the carbinol, which on cyclisation with HPO_3 is converted in small amount into 1 : 2 : 5 : 6-dibenzfluorene. Chloromethyltetrahydronaphthalene, probably a mixture of 1- and 2-derivatives, with $CHMe(CO_2Et)_2$ affords *β-tetrahydronaphthyl-α-methylpropionic acid*, b.p. 157°/0·1 mm., from which, by cyclisation of the acid chloride, is obtained a mixture of ketones, containing 10% of a *ketone*, $C_{14}H_{16}O$, m.p. 80·5—81·5°, oxidised (HNO_3) is mellophanic acid. Treatment of the residual ketones with $Ph\cdot[CH_2]_2\cdot MgCl$ yields a carbinol, dehydrated ($KHSO_4$) to an unsaturated *hydrocarbon*, $C_{22}H_{24}$, b.p. 174°/0·1 mm.; this is cyclised ($AlCl_3$) to a saturated *isomeride*, b.p. 176°/0·15 mm., dehydrogenated (Se) to a *hydrocarbon*, $C_{21}H_{14}$, m.p. 306—308°. F. R. S.

Synthesis of 2-hydroxy- and 2-methyl-3 : 4-benzpyrene. L. F. Fieser and H. Heymann (*J. Amer. Chem. Soc.*, 1941, **63**, 2333—2340).—Succinoylation of 9 : 10-dihydroanthracene with 2·2 mols. of $AlCl_3$ gives only 11% of γ-keto-γ-9 : 10-dihydro-9-anthranylbutyric acid. $Ph\cdot[CH_2]_3\cdot CO_2H$ (not the Et ester in any solvent), $o\text{-}C_6H_4(CO)_2O$, and (best, commercial) $AlCl_3$ in $(CHCl_2)_2$ give 2-*carboxy*-4′-*γ-carboxypropylbenzophenone* (58%), m.p. 149·4—151·6°, hydrogenated, best (90·5%) with Cu chromite in slightly alkaline solution at 200°/3000 lb., to 2-*carboxy*-4′-*γ-carboxypropyldiphenylmethane*, m.p. 141·2—142·4°, which in HF (less well, H_2SO_4) gives γ-9-*anthronyl*-2-n-*butyric acid* (I) (66·5—70%), m.p. 145·4—146·8° (*Me* ester, m.p. 75·8—77·8°). Zn dust in aq. NH_3 at 100° then gives γ-9-anthranyl-*n*-butyric acid (65—72%), m.p. 196·6—198·5°, which with PCl_5 in C_6H_6 and then $SnCl_4$ gives 1′-keto-1′ : 2′ : 3′ : 4′-tetrahydro-1 : 2-benzanthracene (74—80·5%), m.p. 112·8—114·2° (lit. 114—114·5°). With $CH_2Br\cdot CO_2Me$ and Zn in C_6H_6–Et_2O this gives *Me* 1′-*hydroxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-1 : 2-*benzanthracene*-1′-*acetate* (78%), m.p. 139—146° (decomp.), which at the m.p./vac. or with boiling $POCl_3$ or 77% HCO_2H gives the *dehydro-ester* (47—57%) (II), m.p. 148·4—150·4°, and with $SOCl_2$–C_5H_5N–C_6H_6 at 60° gives the *dehydro-acid*, decomp. 241—245°, but, when heated with Pt–C in boiling 1-$C_{10}H_7Me$–CO_2 and then with KOH–EtOH, gives 1 : 2-*benzanthryl*-1′-*acetic acid* (III) (40·5%), m.p. 203·6—204·6°, and 1′ : 2′ : 3′ : 4′-*tetrahydro*-1 : 2-*benzanthryl*-1′-*acetic acid* (IV) (26%), m.p. 209·4—211·4° (*Me* ester, m.p. 77—78·8°). Similar treatment of (II) gives 50·5% of (III) and 15·5% of (IV). H_2–PtO_2 converts (I) in EtOAc into (IV) (24%). Cyclisation of (III) by HF gives 79% of 2-*hydroxy*-3 : 4-*benzpyrene*, decomp. 220° (*acetate*, m.p. 189·6—190·9°), and that of (IV) gives 70% of 2-*keto*-1 : 2 : 8 : 9 : 10 : 10a-*hexahydro*-3 : 4-*benzpyrene* (V), m.p. 137—141°. With MgMeBr, followed by Pd–C in boiling 1-$C_{10}H_7Me$, (V) gives 2-*methyl*-3 : 4-*benzpyrene* (21%), m.p. 167·4—168·4° (*picrate*, m.p. 187·6—188·5°). MgMeCl and (I) in Et_2O–C_6H_6, later boiling C_6H_6, give 17% of γ-9-*methyl*-2-*anthranyl*-n-*butyric acid* (VI), m.p. 151·4—153°, similarly obtained in 10·6% yield from the Me ester, which with LiMe in Et_2O gives the *Me* ester (19%), m.p. 108·2—109·2°, of (VI). M.p. are corr. R. S. C.

Preparation of *o*-4-xylidine. W. A. Wisansky and S. Ansbacher (*J. Amer. Chem. Soc.*, 1941, **63**, 2532).—1 : 2 : 4-$C_6H_3Me_2Br$ (prep. from *o*-xylene in 85% yield), Cu wire, and CuCl in 28—29% aq. NH_3 at 195°/900—1000 lb. give 79% of *o*-4-xylidine. R. S. C.

***NN*-Phenylbenzylhydroxylamine.** W. S. Emerson and C. H. Shunk (*J. Amer. Chem. Soc.*, 1941, **63**, 2485—2486).—$CH_2Ph\cdot NPh\cdot OH$ (*hydrochloride*, m.p. 104—105°; *hydrobromide*, m.p. 96—97°; *Bz* derivative, m.p. 115—117°) with Br in CCl_4 gives N-p-*bromophenyl*-N-*benzylhydroxylamine* (56%), m.p. 164—165° (with H_2–Pt gives *p*-$C_6H_4Br\cdot NH\cdot CH_2Ph$), in boiling 20% H_2SO_4 gives NHPh·OH, and in hot 5% H_2SO_4 gives *p*-$NH_2\cdot C_6H_4\cdot OH$. R. S. C.

Sulphonamides. II. K. N. Gaind, R. P. Sehgal, and J. N. Ray (*J. Indian Chem. Soc.*, 1941, **18**, 209—212).—*p*-$CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot SO_2\cdot NH_2$ with the appropriate amine (2 mols.) in boiling MeOH yields p-*anilino*-, m.p. 196°, -*diethylamino*-, m.p. 153°, -o′-, m.p. 189°, -m′-, m.p. 155°, and -p′-*anisidino*-, m.p. 189°, -o′-, m.p. 212°, -m′-, m.p. 166°, and -p′-*toluidino*-, m.p. 189°, -o′-, m.p. 221°, -m′-, m.p. 173°, and -p′-*phenetidino*-, m.p. 209° (decomp.), -o′-*xylidino*-, m.p. 163°, -p′-*benzeneazoanilino*-, m.p. 261° (decomp.), and (in $C_5H_{11}\cdot OH$) -5′-quinolylamino-acetamidobenzenesulphonamide (*hydrochloride*, m.p. 236°). *p*-$CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot SO_2Cl$ with the amine (4 mols.) in $CHCl_3$ yields p-*diethylaminoacetamidobenzenesulphonyldiethylamide*, m.p. 77°, and *compounds*, *p*-$NHR\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4\cdot SO_2\cdot NHR$, where R = *Ph*, m.p. 202°, o-, m.p. 170°, m-, m.p. 188° (decomp.), and p-*tolyl*, m.p. 296°, and p-*anisyl*, m.p. 185°. A. Li.

Relation between absorption spectra and chemical constitution of dyes. XIX. Mono- and poly-azo-dyes with a single auxochrome. W. R. Brode and L. E. Herdle (*J. Org. Chem.*, 1941, **6**, 713—721).—The absorption spectra of 2 : 4 : 6-tri- and 2 : 4-di-benzeneazophenol, 3 : 5-dibenzeneazo-*p*-cresol, 2- and 4-benzeneazophenol, 3-benzeneazo-*p*-cresol, 3 : 5-di- and *m*-benzeneazophenol, 2 : 4-di- (I), 4- (II) and 2- (III) -benzeneazo-1-naphthol have been determined in 3% NaOH, 95% EtOH, conc. HCl, and, in some cases, in glacial AcOH. In general the absorption curves of polyazo-dyes containing a single auxochrome are composed of the curves of the corresponding azo-compounds in the same solvent with the exception of (I) in 95% EtOH and glacial AcOH. In general, the intensity of absorption of the benzeneazo-compounds is somewhat < the sum of the intensities of the azo-dyes of which they may be considered to be composed. Absorption bands of bisazo-dyes containing a single common auxochrome are broader than those of the corresponding monoazo-dyes. The similarity of the absorption bands of (II) and (III) in alkaline solution and the double additive band of (I) in the same solvent indicate nearly identical resonators with similar auxochromes such as the Na salt of a OH group. The lack of similarity of the absorption bands of (II) and (III) in AcOH and 95% EtOH and their non-additive character to produce the absorption bands of (I) in the same solvent indicate a different type of chromophor in (II) and (III). Such a difference would be predicted on the known H-bonding or chelated resonance ring which is possible in (III) but not in (II). Additional evidence is provided in favour of the theory that the equilibrium between the azoid and quinonoid forms of (II) and (III) is dependent on the

solvent in which they are placed. There is no indication that the benzeneazo-derivatives of the PhOH series exist in a quinonoid form in appreciable quantities in any of these solvents. H. W.

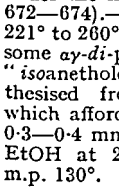
Coupling of *m*-fluorophenol with diazotised amines and the preparation of 2-fluoro-*p*-benzoquinone. H. H. Hodgson and D. E. Nicholson (*J.C.S.*, 1941, 645—646).—*m*-$C_6H_4F{\cdot}OH$ in aq. NaOH appears to couple with ArN_2Cl [Ar = Ph or *p*-$SO_3H{\cdot}C_6H_4$ (slowly) or *m*- or *p*-$NO_2{\cdot}C_6H_4$ (more quickly)] only in the 4-position, to give monoazo-dyes, viz., 3-*fluoro*-4-*benzeneazophenol*, m.p. 139° (decomp.), 4 : 3 : 1-$OH{\cdot}C_6H_3F{\cdot}N_2{\cdot}C_6H_4{\cdot}OH$-*p*, 3-*fluoro*-3′-, m.p. 116°, and -4′-*nitro*-4-*benzeneazophenol*, m.p. 196°, respectively, all of which are reduced by aq. $Na_2S_2O_4$ to 3-*fluoro*-4-*aminophenol*, m.p. 139° (also obtained from 4 : 3 : 1-$NO_2{\cdot}C_6H_3F{\cdot}OH$ and Fe–HCl–EtOH). The latter is oxidised by boiling aq. $FeCl_3$ or by $K_2Cr_2O_7$–aq. H_2SO_4 at <10° to 2-*fluoro*-p-*benzoquinone*, m.p. 80°, which is reduced by NH_2OH or $NHPh{\cdot}NH_2$. A. T. P.

1-Methylphenanthrene series. II. Substitution products. T. Hasselstrom (*J. Amer. Chem. Soc.*, 1941, **63**, 2527—2528; cf. A., 1941, II, 190).—1-Methylphenanthrene and HNO_3 (*d* 1·42) in AcOH at 18°, later 5—10°, give the 9-NO_2-, m.p. 146·5—146·8°, reduced by $Na_2S_2O_4$ in aq. MeOH to the 9-NH_2-derivative, m.p. 138—138·5° (Ac_2 derivative, m.p. 193·7—194·3°), which gives (diazo-reaction) 1-*methyl*-9-*phenanthrol*, m.p. 199·5—200·5° (identified as the known acetate, m.p. 99·5—100·3°), and a trace of a dye, m.p. 283° (decomp.). M.p. are corr. R. S. C.

Isomerides of stilbœstrol. W. H. Linnell and V. R. Sharma (*Quart. J. Pharm.*, 1941, **14**, 259—269).—3′-Amino-4-methoxydeoxybenzoin (from the NO_2-compound and Fe-aq. $FeCl_3$) (diazo-reaction) affords 3′-*hydroxy*-4-*methoxydeoxybenzoin*, converted by EtI–EtOH–KOH into the 3′-*OEt*-compound, m.p. 68—69°, and thence by EtI–EtOH–NaOEt into 4-methoxy-3′-ethoxy-α-ethyldeoxybenzoin. The latter and MgEtI yield γ-anisyl-δ-*m*-phenetylhexan-γ-ol, dehydrated at 100° (bath) (with a little I) to 4-methoxy-3′-ethoxy-αβ-diethylstilbene, which on dealkylation by MgEtI at 135°, then at 165°, affords 3 : 4′-*dihydroxy*-αβ-*diethylstilbene*, m.p. 153—154°. *m*-$NO_2{\cdot}C_6H_4{\cdot}CH_2Cl$ and $AlCl_3$–C_6H_6 yield 3-*nitrodeoxybenzoin*, m.p. 80—91°, reduced by Fe–aq. $FeCl_3$ to the 3-NH_2-compound, m.p. 92—93°, converted (slowly) into the 3-*OH*-compound, m.p. 97—98°, and thence the 3-OMe-derivative, and 3-methoxy-α-ethyldeoxybenzoin, γ-phenyl-δ-*m*-anisylhexan-γ-ol, and 3-methoxy- and 3-*hydroxy*-αβ-*diethylstilbene* (purified through the acetate). 3 : 3′-Dimethoxybenzoin and $SnCl_2$–HCl–EtOH (reflux) give 3 : 3′-dimethoxydeoxybenzoin, b.p. 240—245°/5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 160—160·5°), and thence 3 : 3′-dimethoxy-α-ethyldeoxybenzoin, γδ-di-*m*-anisylhexan-γ-ol, 3 : 3′-dimethoxy- and 3 : 3′-dihydroxy-αβ-diethylstilbene, a glass (3 : 5-*dinitrobenzoate*, m.p. 90—100°). All the αβ-diethylstilbenes prepared are much less active than stilbœstrol. A. T. P.

Bimolecular condensation of *p*-propenylanisole (anethole) under the influence of heat. N. R. Campbell (*J.C.S.*, 1941, 672—674).—Anethole heated under reflux (temp. rises from 221° to 260°) in N_2 for 7 days gives much unchanged material, some αγ-*di*-p-*anisyl*-β-*methylpropane* (**I**), m.p. 71°, and a little "*iso*anethole" (αγ-di-*p*-anisyl-β-methyl-*n*-pentene). (**I**) is synthesised from *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CHMe{\cdot}COCl$–PhOMe–$AlCl_3$, which affords αγ-*di*-p-*anisyl*-β-*methylpropan*-α-*one*, b.p. 180°/0·3—0·4 mm., reduced (Clemmensen) to (**I**). (**I**) and KOH–EtOH at 200° give αγ-*di*-p-*hydroxyphenyl*-β-*methylpropane*, m.p. 130°. A. T. P.

New type of molecular asymmetry. A. Lüttringhaus and H. Gralheer (*Naturwiss.*, 1940, **28**, 255).—A series of quinol decamethylene ethers of type (**I**) have been prepared. These should exist in mirror-image isomerides according as whether the $[CH_2]_{10}$ bridge lies above or below the plane of the C_6 ring. It is supposed that the polymethylene ring is sufficiently narrow, and the substituents are large enough, to hinder the passage of the benzene ring through the larger ring. For very narrow rings the presence of a single substituent is enough to give rise to mol. asymmetry. The prep. of the *compound* when A = CO_2H and B = Br is described. The racemic form has m.p. 114—115°. Resolution by means of the strychnine salt gave the *l*-form, m.p. 154°, $[\alpha]_D^{17}$ −36·7° in $COMe_2$. The acid obtained from the mother-liquor from the strychnine salt gave the *d*-form, $[\alpha]_D^{17}$ +37·5° in $COMe_2$, through the cinchonine salt. Aq. solutions of the Na salts of the active forms retain their rotation after 1 hr. at 90°. 2 : 5-Dibromoquinol $[CH_2]_{10}$ ether has m.p. 94°. A. J. M.



(I.)

Derivatives of pentahydroxybenzene, and a synthesis of pedicellin. W. Baker (*J.C.S.*, 1941, 662—670).—Recorded syntheses of derivatives of $C_6H(OH)_5$ are reviewed. An improved prep. of 1 : 2 : 3 : 5-$C_6H_2(OMe)_4$ (**I**), through the stages 1 : 2 : 3-$C_6H_3(OMe)_3$, 1 : 2 : 6 : 4-$O{:}C_6H_2(OMe)_2{:}O$, and 1 : 4 : 2 : 6-$(OH)_2C_6H_2(OMe)_2$, is recorded. (**I**) and AcCl–$AlCl_3$ in Et_2O at room temp., followed by decomp. of the Al complex with aq. HCl at 100° (bath), afford 2 : 3 : 4 : 6 : 1-$OH{\cdot}C_6H(OMe)_3{\cdot}COMe$ (**II**) (70% yield), oxidised by H_2O_2–aq. NaOH at 20—54° to 1 : 2-*dihydroxy*-3 : 4 : 6-*trimethoxybenzene* (**III**), m.p. 82° (*diacetate*, m.p. 147°), which is methylated by Me_2SO_4–aq. NaOH (+ $Na_2S_2O_4$) at 50—100° to $C_6H(OMe)_5$ (**IV**), m.p. 58—59° (cf. Aulin *et al.*, A., 1937, II, 455). 2 : 3 : 4 : 1-$OH{\cdot}C_6H_2(OMe)_3{\cdot}COMe$ (improved prep.) is oxidised by $K_2S_2O_8$–aq. NaOH at room temp., then refluxing with conc. HCl–C_6H_6, to 2 : 5 : 3 : 4 : 1-$(OH)_2C_6H(OMe)_3{\cdot}COMe$, m.p. 119°. Partial methylation by refluxing with Me_2SO_4–K_2CO_3–C_6H_6 affords 2-*hydroxy*-3 : 4 : 5-*trimethoxyacetophenone*, m.p. 86°, oxidised by alkaline H_2O_2 (in coal gas) to 1 : 2-*dihydroxy*-3 : 4 : 5-*trimethoxybenzene* (**V**), m.p. 90—91° (*diacetate*, m.p. 77°) [methylated to (**IV**)]. 2 : 5 : 4 : 6 : 1-$(OH)_2C_6H(OMe)_2{\cdot}COMe$ refluxed with Me_2SO_4–K_2CO_3–C_3H_6 yields 2-*hydroxy*-4 : 5 : 6-*trimethoxyacetophenone*, b.p. 184—186°/27 mm., oxidised by H_2O_2 to (**V**). (**III**) and aq. $FeCl_3$ at 10° afford 2-*hydroxy*-3 : 6-*dimethoxy*-1 : 4-*benzoquinone* (**VI**), m.p. ~208° (rapid heating), converted by Ac_2O + a trace of H_2SO_4 into the 2-*acetate*, m.p. 147°, which is reduced by aq. $Na_2S_2O_4$ at 60° to 2-*acetoxy*-3 : 6-*dimethoxyquinol*, m.p. 151° [*diacetate* (**VII**), m.p. 114—115°], converted by vigorous methylation in coal gas into (**IV**). (**VI**) and aq. $Na_2S_2O_4$ yield 2-*hydroxy*-3 : 6-*dimethoxyquinol*, m.p. 144° (darkens; rapid heating), converted by $FeCl_3$ or Ac_2O into (**VI**) or (**VII**), respectively. (**II**) and aq. $K_2S_2O_8$–aq. NaOH, then HCl–C_6H_6, yield 2 : 5-*dihydroxy*-3 : 4 : 6-*trimethoxyacetophenone*, m.p. 116—117°, methylated by Me_2SO_4–aq. NaOH–$COMe_2$ at 100° (bath) to 2 : 3 : 4 : 5 : 6-*pentamethoxyacetophenone*, m.p. 43°, b.p. 163°/13 mm. The latter, Na, and EtOBz at 125° or PhCHO–EtOH (+H_2O) at room temp. yield 2 : 3 : 4 : 5 : 6-*pentamethoxydibenzoylmethane*, m.p. 91°, or 2 : 3 : 4 : 5 : 6-pentamethoxyphenyl styryl ketone (pedicellin), m.p. 93°, respectively. (**IV**) and AcCl–$AlCl_3$–Et_2O at room temp. afford 2-*hydroxy*-3 : 4 : 5 : 6-*tetramethoxyacetophenone*, b.p. 183°/14 mm., oxidised by alkaline H_2O_2 (coal gas) at 20—46° to 1 : 2 : 3 : 4 : 5 : 6-$(OH)_2C_6(OMe)_4$ (impure), methylated to $C_6(OMe)_6$. 2 : 3 : 4 : 1-$(OMe)_3C_6H_2{\cdot}COMe$ and $AlCl_3$–Et_2O (12 hr.) yield 2 : 4 : 3 : 1-$(OH)_2C_6H_2(OMe){\cdot}COMe$. 1 : 2 : 4 : 5-$C_6H_2(OMe)_4$ does not react with $AlCl_3$ and AcCl in Et_2O. A. T. P.

Hexamethoxybenzene. (Sir) R. Robinson and C. Vasey (*J.C.S.*, 1941, 660—662; cf. A., 1938, II, 374).—Hydrolysis of 3 : 5-dibromo-2 : 6-dimethoxy-*p*-benzoquinone (**I**) by cold aq. 0·1N-NaOH gives 3 : 5-*dibromo*-6-*hydroxy*-2-*methoxy*-p-*benzoquinone*, m.p. 183°, converted by Zn–AcOH–Ac_2O–NaOAc into 2 : 3 : 5-*triacetoxyanisole*, m.p. 105°. The corresponding trihydroxyanisole, m.p. 119—125°, obtained by HCl–MeOH, is converted by $Zn(CN)_2$–Et_2O–HCl at 0°, then at room temp., into 2 : 3 : 6-*trihydroxy*-4-*methoxybenzaldehyde*, decomp. 199—200°. The constitution of the latter is deduced from the colour reactions of the derived anthocyanidin prepared by condensing with ω : 4-dihydroxy-3 : 5-dimethoxyacetophenone in HCl–EtOAc. Pyrogallolaldehyde and ω : 3 : 4-triacetoxy- or *p*-methoxy-acetophenone and dry HCl–EtOAc afford 3 : 7 : 8 : 3′ : 4′-*pentahydroxy*- (+ $3H_2O$ or anhyd.) or 7 : 8-*dihydroxy*-4′-*methoxy*-*flavylium chloride* (+ H_2O or anhyd.), respectively. (**I**) and MeOH–NaOMe at 100° (bath) yield *tetramethoxy*-p-*benzoquinone*, m.p. 130°, converted by Zn–Ac_2O–AcOH–NaOAc into 3 : 6-*diacetoxy*-1 : 2 : 4 : 5-*tetramethoxybenzene*, m.p. 134°, and thence by HCl–MeOH (in coal gas), followed by aq. NaOH–Me_2SO_4 at 90°, then under reflux, into *hexamethoxybenzene*, m.p. 81°, b.p. ~278° (cf. Aulin *et al.*, A., 1937, II, 455). A. T. P.

Thiocyanation of carcinogenic hydrocarbons. J. L. Wood and L. F. Fieser (*J. Amer. Chem. Soc.*, 1941, **63**, 2323—2331).—The SH and cysteine derivatives previously prepared (A., 1941, II, 10) are not carcinogenic and thus do not function as

intermediates but afford a possible route for metabolic detoxification of the hydrocarbons. The tumour-initiating reaction may consist in reduction of S·S linkings and then conjugation. Carcinogenic hydrocarbons readily react with $(CNS)_2$. Thus, 3 : 4-benzpyrene in CCl_4 at room temp. gives 82% of the 5-*CNS*-derivative (**I**), m.p. 240—240·8° (not obtained from the 5-Cl-derivative by NaCNS in $COMe_2$ at 100°), the structure of which is proved by treatment with Na–EtOH–N_2 to yield the 5-SH derivative which gives the known disulphide and S·CH_2Ph derivative. With 1·1 and 2·2 mols. of $(CNS)_2$ in CCl_4 20-methylcholanthrene gives 41 and 89%, respectively, of the 15-*CNS*-derivative (**II**), m.p. 132° (instantaneous; decomp.), the structure of which is proved by oxidation by $Na_2Cr_2O_7$–AcOH to 6-methyl-1 : 2-benzanthraquinone-5-acetic acid. Boiling 48% HBr does not affect (**I**), but in boiling PhMe, (**II**) decomposes giving HCNS and a *substance* (? a polymeride of 20-methyl-15 : 16-dehydrocholanthrene), m.p. 289—291° (decomp.). With $FeCl_3$ in warm dioxan–MeOH, (**II**) gives a red colour, but (**I**) is unaffected even after several hr. 10-Chloromethyl-1 : 2-benzanthracene (**III**) and NaCNS in boiling $COMe_2$ give 81% of 10-*thiocyanomethyl*-1 : 2-*benzanthracene* (**IV**), m.p. 134·2—135·8°, resolidifies at 137—138°, remelts at 170·2—171° (red colour in warm $FeCl_3$–dioxan–MeOH), converted by CH_2Ph·MgCl in boiling C_6H_6–Et_2O into the known CH_2Ph·S·CH_2 derivative and disulphide. In $COMe_2$ at 100° (**IV**) gives 10-*thiocarbimidomethyl*-1 : 2-*benzanthracene*, m.p. 170·5—171·1° (negative $FeCl_3$ colour), also obtained from (**III**) by NaCNS in $COMe_2$ at 100° and converted (proof of structure) by CH_2Ph·MgCl into the 10-*phenylthioacetamidomethyl* compound, m.p. 186—187° (with hot AcOH–HCO_2H–HBr gives H_2S), by a trace of NaOEt in boiling EtOH into the *thiourethane*, m.p. 167·5—168·9°, and by NH_2Ph at 90° into the as-N-*phenylthiocarbamide*, m.p. 225—227° (decomp.). 10-Methyl-1 : 2-benzanthracene (**V**) barely reacts with 1 mol. of $(CNS)_2$–CCl_4 but with 4·4 mols. gives 56% of the 9-*CNS*-derivative, m.p. 141·5—141·9° (negative $FeCl_3$ test), oxidised to 1 : 2-benzanthraquinone (**VI**) and unchanged in $COMe_2$ at 100°. However, with Br in CS_2, (**V**) gives only the 10-CH_2Br compound. 9-Methyl-1 : 2-benzanthracene and 1·1 mol. of $(CNS)_2$ give 43% of the 10-*CNS*-derivative, m.p. 153—154°, oxidised to (**VI**). For smooth reaction 1 : 2-benzanthracene requires 2·2 mols. of $(CNS)_2$ to give 57% of 10- (**VII**), m.p. 186—187°, and 5% of 9-*CNS*-derivative (**VIII**), m.p. 174·3—174·6° (no $FeCl_3$ colour). With activated Al_2O_3 in C_6H_6, (**VII**) gives the known 10-disulphide, proving its structure. Oxidation of (**VII**) or (**VIII**) gives (**VI**). Anthracene gives only (45%) the 9 : 10-(*CNS*)$_2$ derivative, m.p. 206·7—207·8° (no $FeCl_3$ colour), oxidised to anthraquinone; a mixture from the mother-liquors with Al_2O_3 in C_6H_6 gives 9 : 9′-dianthryl disulphide. 1 : 2 : 5 : 6-Dibenzanthracene does not react with $(CNS)_2$. M.p. are corr. R. S. C.

6-Bromo-3-methoxybenzyl alcohol and [its] derivatives. J. H. Gardner and T. F. McDonnell (*J. Amer. Chem. Soc.*, 1941, **63**, 2279).—6-*Bromo*-3-*methoxybenzyl alcohol*, m.p. 49° [obtained from 3 : 6 : 1-OMe·C_6H_3Br·CHO by $Al(OEt)_3$–EtOH at room temp. or H_2–PtO_2–$FeCl_2$–EtOH], with PCl_3 in $CHCl_3$ gives the *chloride*, m.p. 75·4—76°, and thence by boiling NaOMe–MeOH the *Me ether*, b.p. 126—129°/9 mm. R. S. C.

Influence of substituents on the reactivity of the hydroxyl group in β-phenylethyl alcohol. G. M. Bennett and M. M. Hafez (*J.C.S.*, 1941, 652—659; cf. A., 1935, 453).—*o*- (**I**) or *p*-NH_2·C_6H_4·$[CH_2]_2$·OH (**II**), new m.p. 107° (hydrochloride, m.p. 163°; N-*Ac*, m.p. 105°, and -*Bz* derivative, m.p. 139—140°), affords o-, m.p. 89°, and p-*benzenesulphonamido-β-phenylethyl alcohol*, m.p. 93° (prepared in C_5H_5N), and (diazo-reaction) o-, b.p. 136°/4 mm., and p-*iodo-β-phenylethyl alcohol*, m.p. 48—49°. (**I**) or (**II**) is diazotised, treated with OEt·CS_2K, the ester hydrolysed with aq. KOH–EtOH, and methylated (Me_2SO_4) to o- (**III**), b.p. 165°/12·5 mm., 293°/766 mm. (p-*nitro*-, m.p. 66—67°, and 3 : 5-*dinitrobenzoyl* derivative, m.p. 93°, used for purification; HBr gives the cyclic sulphonium bromide and mechanism of formation is discussed), or p-*methylthiol-β-phenylethyl alcohol* (**IV**), m.p. 37°, b.p. 175°/18 mm., oxidised by H_2O_2–AcOH at 100° (bath) to o-, b.p. 210°/3·5 mm., or p-*methanesulphonyl-β-phenylethyl alcohol*, m.p. 64°, respectively. (**III**) or (**IV**) and $NPhMe_2$–$SOCl_2$ afford o-, b.p. 122°/4 mm. [PhOH at 100° gives a cyclic sulphonium salt and thence *dihydrothionaphthenmethylsulphonium platinichloride*, m.p. 100° (decomp.)], or p-*methylthiol-β-phenylethyl chloride*, b.p. 131°/4 mm., respectively. Methylation (Me_2SO_4–aq. NaOH) of the respective phenol yields o-, b.p. 123°/5 mm., and p-*methoxy-β-phenylethyl alcohol*, m.p. 27·5—28°, b.p. 148—149°/19 mm. Reactivities of the *o*- and *p*-derivatives with HBr are examined to discover which groups cause the special activity of OH previously found in the case of open-chain δ-OH-sulphides. No outstanding difference in reactivity is noted, except in the case of (**III**), which reacts 620 times as fast as does (**IV**). Theoretical considerations are discussed. The high reactivity of the OH in (**I**) is shown by reaction with $ArSO_2Cl$. Thus, (**I**) and *p*-C_6H_4Me·SO_2Cl or $PhSO_2Cl$ in 10% aq. NaOH give a little *p*-toluene- or benzene-sulphonylindoline, respectively; AcCl or BzCl gives no cyclic product. Ph·$[CH_2]_2$·OH is unchanged with $PhSO_2Cl$ in 10% aq. NaOH at room temp. *o*-Benzamido- (**V**) or -acetamido-*β*-phenylethyl alcohol and $PhSO_2Cl$–aq. NaOH–$COMe_2$ give *N*-benzoyl (**VI**)- or -acetyl-indoline (**VII**), respectively. *o*-Benzenesulphonamidophenylethyl alcohol gives only a little benzenesulphonylindoline, being mainly unchanged. (**V**) and $NPhMe_2$–$SOCl_2$–$CHCl_3$ afford *o-benzamido-β-phenylethyl chloride*, m.p. 119·5°, converted by NaOH–$COMe_2$ into (**VI**). The hydrochloride of (**I**) and AcCl–C_5H_5N yield *o-acetamido-β-phenylethyl chloride*, m.p. 120°, convertible into (**VII**). A. T. P.

Factors determining the course and mechanisms of Grignard reactions. I. Effects of metallic compounds on some Grignard–carbonyl interactions. M. S. Kharasch, (Miss) S. C. Kleiger, J. A. Martin, and F. R. Mayo. **II. Effect of metallic compounds on the reaction between *iso*phorone and magnesium methyl bromide.** M. S. Kharasch and P. O. Tawney. **III. Effect of metallic halides on the reactions between benzophenone and magnesium methyl bromide.** M. S. Kharasch and F. L. Lambert (*J. Amer. Chem. Soc.*, 1941, **63**, 2305—2307, 2308—2315, 2315—2316).—I. Production of $CHPh_2$·OH (**I**) (>90%) from $COPh_2$ by MgBu$^\beta$Br (prep. from purest Mg) is unaffected by CuCl (up to 1 mol.-%), but presence of $MnCl_2$ leads to $(CPh_2$·$OH)_2$, the amount thereof increasing with the amount of $MnCl_2$ used up to 2 mols.-% [only a trace of (**I**) then formed]. $CrCl_2$ and $FeCl_3$ give similar, but less pronounced, results. The catalysed reaction has a chain mechanism. Much tar is formed from CCl_3·CHO by MgMeI, but the yield of isolable CCl_3·CHMe·OH is increased by $MnCl_2$ or Mn and reduced much by $FeCl_3$ and a little by CuCl.

II. Addition of *iso*phorone (**II**) to MgMeBr in Et_2O gives 1 : 3 : 5 : 5-*tetramethyl*-Δ^3-cyclo*hexenol* (**III**) (42·6%), b.p. 59—60°/5 mm., and 1 : 3 : 5 : 5-tetramethyl-$\Delta^{1:3}$-*cyclo*hexadiene (**IV**) (48·2%), b.p. 24—25°/7 mm. (cf. Hess *et al.*, A., 1918, i, 291) (the reverse order of addition gives 67·2 and 23·6%, respectively), but presence of salts (1 mol.-% unless otherwise stated) often greatly affects the reaction. Thus, 0·2 or 1 mol.-% of $FeCl_3$ leads to (**III**) 5·7, 0, (**IV**) 8·85, 2·2, 3 : 3 : 5-*trimethyl*-Δ^4-cyclo*hexenone* or -$\Delta^{1:5}$-cyclo*hexadienol* (**V**) (b.p. 32°/3·5 mm., 181—185°/750 mm.) 66·4, 81·6, and 1 : 1′-dihydroxy-3 : 5 : 5 : 3′ : 5′ : 5′-hexamethyldi-Δ^2-*cyclo*hexenyl (**VI**) (m.p. 161—162°) 5·26, 9·46%, respectively. CuCl leads to (**IV**) 6·96 and, by 1 : 4-addition, 3 : 3 : 5 : 5-*tetramethyl*cyclo*hexanone* (**VII**) (b.p. 59—61°/5·5, 196—197°/760 mm.) 82·5%. $NiCl_2$ leads to (**III**) 22·6, (**IV**) 7·3, and (**VI**) 61·1%. $CoCl_2$ under various conditions leads to (**III**) 0—13·8, (**IV**) 0—20·0, and (**VI**) 67·0—78·5%. Pure Mg (20 mol.-% excess) leads to (**III**) 22·7, (**IV**) 55·5, and (**VI**) 1·45%; ordinary Mg leads to (**III**) 4·35, (**IV**) 85·5, and (**VII**) 1·45%. Cu powder leads to (**IV**) 78·0 and (**VII**) 8·0%. AgCl leads to (**III**) 35·0 and (**IV**) 57·7%. $PbCl_2$ leads to (**IV**) 85·7% and (**VI**) a trace. $CrCl_3$ leads to (**III**) 27·4, (**IV**), 56·8%, and (**VII**) a trace. VCl_3 leads to (**III**) 56·7 and (**IV**) 33·1%. $MnCl_2$ leads to (**III**) 28·5 and (**IV**) 56·0%. Dehydration of (**III**) to (**IV**) occurs readily if (**III**) is impure, kept in air, or distilled (best with a little anhyd. $KHSO_4$). The structure of (**IV**) follows by analogy, from formation of *adducts*, m.p. 98—99° and 133·5—134·5°, with $(CH{\cdot}CO)_2O$ in boiling C_6H_6 and α-naphthaquinone in boiling 95% EtOH, respectively. (**IV**) yields a cryst., unstable dibromide and is stable only in absence of air. (**VII**) yields an *oxime*, m.p. 144—145°, *semicarbazone*, m.p. 217—218° (decomp.), 2 : 4-*dinitro*-, m.p. 133—134°, and p-*nitrophenylhydrazone*, m.p. 176·5—177·2°, and is stable to $KMnO_4$. Evidence for the structure of (**V**) is inconclusive. Physical consts. and the faster absorption of O_2 differentiate (**V**) from (**II**), into which, however, it passes slowly when kept; the change is accelerated by a trace of AcOH and $KHSO_4$ and is very rapid when (**V**) is distilled from $KHSO_4$; its progress

is followed by observing the change in *n*. 3 : 5 : 5-*Trimethyl*-Δ^1-*cyclohexenol*, b.p. 69°/5 mm. [benzoate, b.p. 134—136°/5 mm. (slight decomp.); *p-nitrobenzoate*, m.p. 68·5—69·5°], is obtained from (II) by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$; it gives no CO derivatives, but (V) gives a *semicarbazone*, m.p. 186—187°, also obtained much less readily from (II), and an oxime, m.p. 78—79° [depressed to 50—52° by the oxime (m.p. 78—79°) obtained from (II)]. (V) gives no $FeCl_3$ colour.

III. $COPh_2$ and MgMeBr give only $CPh_2Me{\cdot}OH$ and addition of 2 mol.-% of Mg, CuCl, or $MnCl_2$ is without effect, but 2 mol.-% of $FeCl_3$ or $CoCl_2$ leads to $CPh_2Me{\cdot}OH$ 21 or 2 and $(CPh_2{\cdot}OH)_2$ 65 or 93%, respectively. R. S. C.

Hydrogenation of acetylenic compounds. Di-*p*-tolylbutinenediol diacetate. A. I. Nogaideli and K. J. Dzagnidze (*J. Gen. Chem. Russ.*, 1941, **11**, 136—139).—*p*-$C_6H_4Me{\cdot}CHO$ is added to $(:C{\cdot}MgBr)_2$ in Et_2O (24 hr. at room temp.), to yield a mixture of stereoisomerides of *αδ-di*-p-*tolyl*-Δ^{β}-*butinene-αδ-diol*, m.p. 122—123° (I) and 169—170°. The *diacetate*, m.p. 76—78°, of (I) is hydrogenated (Pd catalyst) to *αδ-di*-p-*tolyl*-Δ^{β}-*butene-*, m.p. 75—77°, and *-butane-αδ-diol diacetate*, m.p. 78·5—80·5°. R. T.

Kluyver's inosose and the configuration of *meso*-inositol and of scyllitol. T. Posternak (*Arch. Sci. phys. nat.*, 1941, [v], **23**, *Suppl.*, 44—47).—*meso*-Inositol (I) is oxidised by *Acetobacter suboxydans* to an inosose (II), m.p. 198—200° (cf. Kluyver *et al.*, A., 1940, III, 75), which with Ac_2O–conc. H_2SO_4 (or anhyd. $ZnCl_2$) gives a *penta-acetate*, m.p. 211° and 147° (two forms). (I) with conc. HNO_3 yields inosose (cf. Posternak, A., 1937, II, 65) (penta-acetate, m.p. 106—108°). All three penta-acetates with C_5H_5N or NaOAc readily yield 1 : 2 : 3 : 5-$C_6H_2(OH)_4$. Controlled oxidation of (II) with $KMnO_4$–Na_2CO_3 yields *dl*-saccharic acid, which establishes the configuration of (II). When (II) is reduced (H_2–PtO_2) it yields (I) quantitatively, which establishes the structure of (I). Reduction of (II) with Na–Hg in AcOH yields (I) and scyllitol, isomeric reduction products. J. L. D.

Tervalent carbon. I. Diphenylcarbethoxymethyl radical. B. Witten and F. Y. Wiselogle (*J. Org. Chem.*, 1941, **6**, 584—595).—$CPh_2Cl{\cdot}CO_2Et$ is converted by "mol. Ag" in Et_2O–C_6H_6 at 60—80° under N_2 or by Hg in C_6H_6–Et_2O at room temp. into Et_2 tetraphenylsuccinate (I), m.p. 90—94° to a yellow liquid after softening at 80°. (I) is colourless, stable, and inert when dry. Its solutions are pale yellow at room temp.; the intensity of absorption increases on warming but the colour fades when the solution is cooled. When exposed to air (I) gives *diphenylcarbethoxymethyl peroxide*, colourless, m.p. 116—118° (decomp.), hydrolysed by KOH–MeOH to $OH{\cdot}CHPh_2{\cdot}CO_2H$. HCl in C_6H_6 rearranges (I) to *Et* p-*α-carbethoxybenzyltriphenylacetate*, m.p. 88—89°, hydrolysed by KOH–MeOH to *Et* p-*α-carboxybenzyltriphenylacetate* (II), m.p. 206—207°, or by an excess of alkali to p-*α-carboxybenzyltriphenylacetic acid* (III); m.p. 287—291° (decomp.), also obtained from (II). (II) is oxidised by CrO_3 in boiling AcOH to *Et* p-*benzoyltriphenylacetate*, m.p. 126—127°; under similar conditions (III) yields terephthalophenone. In the presence of pyrogallol (IV) the amount of O_2 absorbed by (I) corresponds with 2 mols. of gas for each mol. of (I). The change is unimol., the rate of absorption being $\propto$ concn. of (I) but independent of pressure of O_2 or concn. of (IV). The rate-controlling step is the dissociation of (I); the peroxy-radicals $R{\cdot}O{\cdot}O{\cdot}$ are rapidly destroyed by (IV) but the ultimate reaction products have not been identified. The half-life of (I) in *o*-$C_6H_4Cl_2$ at 0° is 8·47 min. and the energy of activation is 23·3 kg.-cal. The rate of dissociation of (I) exceeds that of any other diacyltetraphenylethane yet studied and, at 0°, is practically identical with that of C_2Ph_6; it far exceeds that of the structurally similar dixanthyl-9 : 9′-dicarboxylic acid or its Me_2 ester. H. W.

Reactions of *p*-bromocinnamic acid. (Misses) M. Reimer and E. Tobin (*J. Amer. Chem. Soc.*, 1941, **63**, 2490—2493).—*p*-$C_6H_4Br{\cdot}CH{:}CH{\cdot}CO_2H$ (I) (prep. in 94% yield from *p*-$C_6H_4Br{\cdot}CH{:}CH{\cdot}CO{\cdot}CO_2H$ by H_2O_2–Na_2CO_3; excellent also for other cinnamic acids), m.p. 257° (cf. lit.), and Br in, best, boiling CCl_4 give the *dibromide* (II) (88%), m.p. 192° (*Me* ester, m.p. 110°). In boiling H_2O, (II) gives slowly *p*-$C_6H_4Br{\cdot}CHO$, (I), and *p*-$C_6H_4Br{\cdot}CH{:}CHBr$, m.p. 81°, in boiling 2% aq. Na_2CO_3 gives *α*: *p-dibromostyrene* (70%), m.p. 74° (odour of mint), and in 25% KOH–MeOH at room temp. gives *cis-α*: *p-dibromocinnamic acid* (nearly 100%), softens at 145°, m.p. 148° (*Me* ester, m.p. 57°), which at 160° and later 220° gives slowly the *trans*-isomeride, m.p. 221° (A., 1940, II, 374). In boiling 25% KOH–MeOH, (II) gives p-*bromophenylpropiolic acid* (III) (80%), m.p. 201° (*Me* ester, m.p. 106°), also obtained with (I) from (II) at 194° and converted by 98% H_2SO_4 into *β-keto-β*-p-*bromophenylpropionic acid* (90%), softens at 120°, m.p. 123—125° [decomp. to *p*-$C_6H_5Br{\cdot}COMe$ (odour of trailing arbutus)] (*Me* ester, m.p. 45—46° after softening; red $FeCl_3$ colour). Br and (III) in $CHCl_3$ give isomeric *αβ*: *p-tribromocinnamic acids*, colourless, m.p. 166—167° (*Me* ester, m.p. 69°), and yellow, m.p. 153—154° (softens ~145°) (*Me* ester, m.p. 67°), both dehydrated by P_2O_5 to 2 : 3 : 6-tribromoindone. With Br in H_2O or aq. Na_2CO_3, (III) gives *α-bromo-β*-p-*bromophenylacetylene* (odour of anise), m.p. 102°, converted by 98% H_2SO_4 into *p*-$C_6H_4Br{\cdot}CO{\cdot}CH_2Br$. R. S. C.

Esterification of sterically hindered acids. M. S. Newman (*J. Amer. Chem. Soc.*, 1941, **63**, 2431—2435).—Sterically hindered benzoic acids are readily esterified by addition of their solution in 100% H_2SO_4 to ROH (not $Bu^{\gamma}OH$). The esters are hydrolysed by addition of their solution in 100% H_2SO_4 to H_2O. Thus are prepared (and hydrolysed) *Me*, b.p. 114·8—115·2°/7—7·5 mm., *Et*, b.p. 115°/6—6·5 mm., and Pr^{β} 2 : 4 : 6-*trimethylbenzoate*, b.p. 120·2—121°/6—6·5 mm., *Me* 2 : 4 : 6-*tri-ethyl-*, b.p. 93·2—93·8°/0·5—1 mm., and *-isopropyl-benzoate*, m.p. 37—38·4°, b.p. 99·6—100·4°/0·5—1 mm. BzOH and ROBz do not undergo these reactions. The reasons, discussed in detail, for the differences lie in the stability (resonance) of the RCO^+ ion present in the H_2SO_4 solutions. R. S. C.

6-Bromo-2-methoxy-1-naphthoic acid. F. L. Warren, M. Gindy, and F. G. Baddar (*J.C.S.*, 1941, 687—688).—2 : 1-$OMe{\cdot}C_{10}H_5{\cdot}CO_2H$, m.p. 176—177° (lit. 176° and 133—134°) (from 2-$OMe{\cdot}C_{10}H_6{\cdot}CHO$–$KMnO_4$–aq. Na_2CO_3–$COMe_2$) and Br–AcOH yield 1 : 2-$C_{10}H_5Br{\cdot}OMe$; 2 : 1-$OMe{\cdot}C_{10}H_5{\cdot}CO_2Me$, however, similarly affords *Me* 6-*bromo*-2-*methoxy*-1-*naphthoate*, m.p. 112·5°, hydrolysed by KOH–EtOH to 6-*bromo*-2-*methoxy*-1-*naphthoic acid*, m.p. 176—177°. Decarboxylation (Cu-bronze–quinoline) yields 6 : 2-$C_{10}H_6Br{\cdot}OH$ and 6 : 2-$C_{10}H_6Br{\cdot}OMe$. A. T. P.

2-Alkyl 1-dialkylaminoalkyl 3-aminophthalates as local anæsthetics. F. F. Blicke and C. Otsuki (*J. Amer. Chem. Soc.*, 1941, **63**, 2435—2436).—1 : 3 : 2-$CO_2H{\cdot}C_6H_3(NO_2){\cdot}CO_2R$ [prep., usually, from 3 : 1 : 2-$NO_2{\cdot}C_6H_3(CO)_2O$ (1 mol.) and ROH (5 mols.) at 100°] and $NEt_2{\cdot}[CH_2]_2{\cdot}Cl$, usually in $Pr^{\beta}OH$ at 100°, give 2-*Me*, m.p. 145—146°, *-Et*, m.p. 126—128°, *-Pr*$^{\alpha}$, m.p. 111—112°, *-Pr*$^{\beta}$, m.p. 124—126°, *-Bu*$^{\alpha}$, m.p. 80—82°, *-Bu*$^{\beta}$, m.p. 125—126°, -CHMeEt (corresponding *hydrobromide*, hygroscopic), -n-*amyl*, m.p. 71—73°, -n-*hexyl-*, m.p. 64—66°, -n-*dodecyl*, m.p. 84—86°, and -n-*octadecyl*, m.p. 89—90°, 1-*β-diethylaminoethyl* 3-*nitrophthalate hydrochloride*, reduced to 2-*Me*, m.p. 150—152°, *-Et*, m.p. 139—140°, *-Pr*$^{\alpha}$, m.p. 129—130°, *-Pr*$^{\beta}$, m.p. 153—154°, *-Bu*$^{\alpha}$, m.p. 117—118°, *-Bu*$^{\beta}$, m.p. 118—119°, -CHMeEt (corresponding *hydrobromide*, m.p. 117—118°), -n-amyl (I) (corresponding *hydrobromide*, m.p. 86—88°), -n-hexyl (II) (corresponding *citrate*, m.p. 72—74°), -n-dodecyl (corresponding *citrate*, m.p. 84—86°), and -n-octadecyl 1-*β*-diethylaminoethyl 3-aminophthalate hydrochloride (free *base*, m.p. 45—46°). Similarly are prepared 2-Pr$^{\alpha}$ 1-*γ*-piperidino-*n*-propyl (*hydrobromide*, m.p. 137—139°), 1-*γ*-dibutylamino-*n*-propyl (*methiodide*, m.p. 155—156°), and 1-*γ*-dimethylamino-*ββ*-dimethyl-*n*-propyl (*methiodide*, m.p. 164—165°) 3-nitrophthalate, reduced to 2-Pr$^{\alpha}$ 1-*γ*-piperidino-*n*-propyl (*hydrochloride*, m.p. 123—124°), 1-*γ*-dibutylamino-*n*-propyl (*hydrobromide*, m.p. 115—116°), and 1-*γ*-dimethylamino-*ββ*-dimethyl-*n*-propyl (*hydrobromide*, m.p. 139—141°) 3-aminophthalate. *γ-Dibutylamino*-n-*propyl chloride aurichloride* has m.p. 143—146°. Salts of (I) and (II) are very potent local anæsthetics. R. S. C.

1-Alkyl 2-dialkylaminoalkyl 4-aminophthalates as local anæsthetics. F. F. Blicke and E. R. Castro (*J. Amer. Chem. Soc.*, 1941, **63**, 2437—2439).—2 : 4 : 1-$CO_2H{\cdot}C_6H_3(NO_2){\cdot}CO_2R$ (R = Me, Et, Pr$^{\alpha}$, m.p. 73—75°, Pr$^{\beta}$, m.p. 149—150°, Bu$^{\alpha}$, an oil, *Bu*$^{\beta}$, m.p. 108—109°, *CHMeEt*, m.p. 112—114°) is obtained from 4 : 1 : 2-$NO_2{\cdot}C_6H_3(CO)_2O$ (I) (0·3 mol.) and ROH (5 mols.) at 100° and with $NEt_2{\cdot}[CH_2]_2{\cdot}Cl$ gives 1-*Me*, m.p. 164—165°, *-Et*, m.p. 143—144°, *-Pr*$^{\alpha}$, m.p. 146—147°, *-Pr*$^{\beta}$, m.p. 136—137°, -Bu$^{\alpha}$ (corresponding *hydrobromide*, m.p. 116—117°), *-Bu*$^{\beta}$, m.p. 105—106°, and *-CHMeEt*, m.p. 132—133°, 2-*β-diethylaminoethyl* 4-*nitrophthalate hydrochloride*.

$OH{\cdot}[CH_2]_2{\cdot}Hal$ and (I) in boiling C_6H_6 give 2-*β-bromo-*, m.p.

99—101°, and 2-*β-chloro-ethyl II* 4-*nitrophthalate*, m.p. 97—98°, the acid chloride ($SOCl_2$) of which with ROH gives 1 : 4 : 2-$CO_2R{\cdot}C_6H_3(NO_2){\cdot}CO_2{\cdot}[CH_2]_2{\cdot}$Hal (oils) and thence ($NHEt_2$–PhMe; 95°) the above-named dialkyl esters and 1-*Et* 2-*β-dipropylamino-*, m.p. 143—144°, *-piperidino-*, m.p. 155—156°, and *-morpholino-ethyl* 4-*nitrophthalate hydrochloride*, m.p. 120—121°. Reduction by $SnCl_2$–HCl–AcOH gives 1-Me (*hydrochloride*, m.p. 166—168°), -Et (*hydrochloride*, m.p. 152—153°), -Pr$^\alpha$ (*hydrobromide*, m.p. 117—118°), -Pr$^\beta$ (*citrate*, m.p. 97—99°), -Bu$^\alpha$ (*citrate*, m.p. 93—94°), -Bu$^\beta$ (*citrate*, m.p. 102—104°), and -CHMeEt (**II**) (*benzyloiodide*, m.p. 79—83°) 2-diethylaminoethyl 4-aminophthalate and 1-*Et* 2-*β-dipropylamino-*, m.p. 114—116°, *-piperidino-*, m.p. 182—183°, and *-morpholino-*, m.p. 181—182°, *-ethyl* 4-*aminophthalate hydrochloride*. The most active product, (**II**), is less active than 2 : 3 : 1-$CO_2R{\cdot}C_6H_3(NH_2){\cdot}CO_2{\cdot}[CH_2]_2{\cdot}NR'_2$. R. S. C.

Synthesis of aldehydes from Grignard reagents. II. Polymethylbenzaldehydes. L. I. Smith and J. Nichols (*J. Org. Chem.*, 1941, **6**, 489—506).—Examination of the literature suggests that the most suitable initial materials for the prep. of aldehydes from Grignard reagents are $CH(OEt)_3$ (**I**), NPh:CH·OEt (**II**), and S_2-acids (**III**) and these substances have been used in the comparative prep. of *o-* and *p*-$C_6H_4Me{\cdot}CHO$, 2 : 4 : 5-, 2 : 4 : 6-, and 2 : 3 : 6-$C_6H_2Me_3{\cdot}CHO$, 2 : 3 : 5 : 6- and 2 : 3 : 4 : 6-$C_6HMe_4{\cdot}CHO$, and $C_6Me_5{\cdot}CHO$. With (**I**) the best results are obtained by heating the mixture for 5 hr. under reflux followed by cautious removal of Et_2O on the steam-bath. During this process a point is reached at which a vigorous reaction sets in; although this is liable to become uncontrollable, the yields of aldehyde are substantially reduced if it does not occur. It is therefore difficult to work with >0·1—0·2 mol. of material. Otherwise it is an admirable synthesis, the materials being cheap, the yields excellent, and the procedure simple. It is particularly suitable for use with costly aromatic halides especially when the " entrainment " method has to be used for the prep. of the Grignard reagent. With (**II**) the yields of aldehyde exceed those with (**I**) by 4—17% and the reaction is sufficiently moderate to permit the use of large amounts of material. (**II**) is expensive and somewhat difficult to obtain dry whilst impurities in (**II**) very greatly depress the yields. The synthesis with (**III**) is inferior to that with (**I**) or (**II**) and the varied yields are difficult to explain.

An unsubstituted position *ortho* to CHO allows for ease and rapidity of formation of the additive compound with $NaHSO_3$ and under these conditions the presence of a *p*-substituent has little, if any, effect. In a di-*o-* substituted aldehyde with a free *para* position addition does not occur rapidly but good yields of product are obtained after sufficient time. If both *o-* and the *p*-positions are occupied, the additive compound is formed with difficulty and in very small yield. No additive compound is obtained with the completely substituted aldehyde. The activation of CHO by the free *p*-position or the deactivation by a substituted *p*-group is shown by the ease with which these aldehydes undergo auto-oxidation. The following are new : 2 : 3 : 6-*trimethylbenzaldehyde*, b.p. 113—114°/10 mm., 115—116°/12 mm. (*oxime*, m.p. 124—126°; *semicarbazone*, m.p. 167—169°); 2 : 3 : 4 : 6-*tetramethylbenzaldehyde*, b.p. 136°/10 mm., f.p. 15° [*oxime*, ? two forms, m.p. ~100° and 136—137°; *semicarbazone*, m.p. 183—185° and 218—221° (decomp.) after resolidification]; 2 : 3 : 5 : 6-*tetramethylbenzaldehyde*, b.p. 135°/11 mm., f.p. 20° [*oxime*, m.p. 124·5—125·5°; *semicarbazone*, becomes waxy at 205—210° and melts at 268—270° (decomp.)]. H. W.

Action of potassamide on *syn-* and *anti*-aldoximes, their *O*-methyl ethers and their acetyl derivatives. G. Vermillion and C. R. Hauser (*J. Org. Chem.*, 1941, **6**, 507—515).—KNH_2 in liquid NH_3 at room temp. causes complete decomp. of *anti-p*-OMe·C_6H_4·CH:N·OH (**I**) within 9 days, giving the corresponding amidine (**II**) (isolated as the picrate, 48%) and amide (**III**) (15%). Under similar conditions the *syn*-aldoxime appears to be partly decomposed but the products were not isolated. (**I**) probably loses H_2O giving the nitrile (**IV**), which is converted by KNH_2 into (**II**). (**III**) is probably formed by hydrolysis of (**II**) and also by the action of KOH on (**IV**). In presence of KNH_2 in liquid NH_3 at −33° *syn-* and *anti-p*-OMe·C_6H_4·CH:N·OMe give *p*-OMe·C_6H_4·CN apparently quantitatively. Under similar conditions *syn-* and *anti*-CHPh:N·OAc give nitrile (**V**) and the corresponding *syn-* and *anti*-aldoxime, reactions appearing to be complete within 10 min. The *anti*-acetates give higher yields of (**V**) and lower yields of aldoxime than do the *syn*-isomerides. The mechanisms of elimination reactions are discussed. H. W.

Condensation of aldehydes with amides. VII. Condensation of piperonal. VIII. Condensations of 6-nitropiperonal. K. C. Pandya and P. G. Varghese (*Proc. Indian Acad. Sci.*, 1941, **14**, **A**, 18—24, 24—28).—VII. Piperonal (**I**) condenses with acid amides best when the reactants are heated together without C_5H_5N. Under a variety of conditions $HCO{\cdot}NH_2$ does not condense. The products are all of the benzylidenediamide type resembling those derived from the methoxybenzaldehydes. The yields vary between 38% and 77%. The following are described : *piperonylidenedi-benzamide*, m.p. 222°, which does not decolorise Baeyer's reagent or Br in $CHCl_3$ and is hydrolysed by boiling 2N-H_2SO_4 to NH_2Bz and (**I**); *-acetamide*, m.p. 237—238°; *-propionamide*, m.p. 225°, *-phenylacetamide*, m.p. 224°, *-cinnamamide*, m.p. 248°, *-n-butyramide*, m.p. 208°, and *n-heptoamide*, m.p. 163°.

VIII. The products obtained from 6-nitropiperonal and acid amides resemble those derived from (**I**). In the case of NH_2Ac and CHPh:CH·$CO{\cdot}NH_2$ the yields are distinctly > those with (**I**) but in the other cases the reaction is slower and the yields are poorer. $HCO{\cdot}NH_2$ does not condense. The following are described : 6-*nitropiperonylidenedi-acetamide*, m.p. 235°, *-propionamide*, m.p. 212°, *-n-butyramide*, m.p. 209° (decomp.), *-n-heptoamide*, m.p. 185°, *-benzamide*, m.p. 248°, *-phenylacetamide*, m.p. 231°, and *-cinnamamide*, m.p. 232°. H. W.

Oxidation of alcohols and ketones. H. Adkins and R. C. Franklin (*J. Amer. Chem. Soc.*, 1941, **63**, 2381—2383).—The utility of ketones for oxidation of alcohols in presence of $Al(OBu^\gamma)_3$ is discussed and investigated for, *e.g.*, $CHPh_2{\cdot}OH$, cholesterol, *cyclo*hexanols, and $CH_2Bu^\gamma{\cdot}OH$. Relevant factors are the oxidation potential of the ketones, the rates of oxidation and condensation, and the ease of separation of the products. COMeEt and *cyclo*hexanone are best for oxidation of sterols; Bz_2 and *p*-O:C_6H_4:O or Bz_2 are best for prep. of ketones of b.p. <100° and 100—200° respectively. R. S. C.

Keten in the Friedel–Crafts reaction. II. Use of mixed acetic anhydrides. J. W. Williams, Y. J. Dickert, and J. A. Krynitsky (*J. Amer. Chem. Soc.*, 1941, **63**, 2510—2511; cf. A., 1940, II, 90).—Addition of crude RCO·O·COMe (**I**) (1 mol.; prep. from RCO_2H and keten) to C_6H_6 (excess) and $AlCl_3$ (3·2 mols.) gives exothermally and later at 100° COPhMe and COPhR in the following respective yields : R = Et 56·0, 38·7, Pr$^\alpha$ 33·8, 66·2, Pr$^\beta$ 55·2, 57·9, Bu$^\alpha$ 42·2, 67·8, Bu$^\beta$ 35·5, 66·6, Bu$^\gamma$ 35·8, 25·3, *n*-amyl 39·2, 59·2, *n*-$C_{17}H_{35}$ 33·5, 10·7, and Ph 23·3, 14·2%. Some AcOH is always obtained in the prep. of (**I**), particularly if an excess of RCO_2H is present, by the reaction RCO·O·COMe + $RCO_2H \rightarrow (RCO)_2O$ + AcOH. The stated proportions of reactants give max. yields. R. S. C.

Syntheses with 2-bromo-5-nitroacetophenone. W. Borsche and A. Herbert (*Annalen*, 1941, **546**, 293—303).—*o*-$C_6H_4Br{\cdot}CN$ and MgMeBr give *o*-$C_6H_4Br{\cdot}COMe$ (2 : 4-dinitrophenylhydrazone, m.p. 188—189°) in ~80% yield, which yields 5 : 2 : 1-$NO_2{\cdot}C_6H_3Br{\cdot}COMe$ (**I**), m.p. 87° (2 : 4-*dinitrophenylhydrazone*, m.p. 211°). (**I**) is transformed by Cu powder at 220° into 3-*keto*-1-*methyl*-4′ : 4″-*dinitrodibenzo*-$\Delta^{1:4:6}$-*cycloheptatriene*, m.p. 195° (2 : 4-*dinitrophenylhydrazone*, m.p. 295°). (**I**), PhCHO, and 2·5N-NaOH in EtOH at room temp. give 2-*bromo*-5-*nitrophenyl styryl ketone* (**II**), m.p. 106° [2 : 4-*dinitrophenylhydrazone*, m.p. 254—256° (slight decomp.)], with some *αε-diketo-γ-phenyl-αε-di*-2-*bromo*-5-*nitrophenylpentane*, m.p. 160°. (**II**) and NH_2OH in AcOH do not give the expected oxime but, probably, *nitrohydroxylaminophenyl styryl ketoxime*, softens with slight decomp. at ~360°. With N_2H_4,H_2O in boiling EtOH (**I**) gives 5-*nitro*-3-*methylindazole*, m.p. 213°. (**I**) and NH_3–EtOH at 100° smoothly yield 5 : 2 : 1-$NO_2{\cdot}C_6H_3(NH_2){\cdot}COMe$ (**III**), m.p. 151—152° [2 : 4-*dinitrophenylhydrazone*, decomp. 306°; *Ac* derivative, m.p. 152—153°, hydrolysed to (**III**) by NaOH; *Bz* compound, m.p. 193°, transformed by NaOH into (**III**) and 6-*nitro*-2-5′-*nitro*-2′-*aminophenyl*-4-*methylquinoline*, m.p. 320° (decomp.), also obtained by the action of NaOH in aq. EtOH on (**III**)]. $CH_3Ac{\cdot}CO_2Et$ and (**III**) at 160—170° afford 6-*nitro*-2-*keto*-3-*acetyl*-4-*methyl*-1 : 2-*dihydroquinoline*, m.p. 340—341° (decomp.). $CH_2(CO_2Et)_2$ and (**III**) at 170° give the *compound*, $C_{19}H_{14}O_7N_4$, m.p. 326° (decomp.), and *Et* 6-*nitro*-4-*methylcarbostyryl*-3-*carboxylate*, m.p. 300°. Addition of $NaNO_2$ to (**III**) in AcOH containing H_2SO_4 leads to 6-*nitro*-4-*hydroxy-*

cinnoline, $NO_2 \cdot C_6H_3 < \begin{matrix} C(OH):CH \\ N=\!=\!=N \end{matrix}$, m.p. 343—344°. Br and (**III**) in $CHCl_3$ in subdued daylight give *5-nitro-2-aminophenacyl bromide*, m.p. 164—165° (*Ac* derivative, m.p. 150—152°, transformed by the action of Na_2CO_3 and air in aq. EtOH into 5 : 5′-*dinitroindigotin*, m.p. >375°). H. W.

Orientation in the Fries rearrangement of phenyl octoate. A. W. Ralston, M. R. McCorkle, and E. W. Segebrecht (*J. Org. Chem.*, 1941, **6**, 750—763; cf. A., 1941, II, 66).—A study has been made of the partly completed and complete rearrangements of Ph octoate (**I**) in the presence of varying mol. proportions of $AlCl_3$ and of such $AlCl_3$ complexes as are considered likely to be present in the rearrangement of (**I**). Experiments are mainly performed in $(CHCl_2)_2$ at 100° but some are also done at other temp. and also in the absence of solvent. When approx. equal mol. proportions or less of $AlCl_3$ are employed the val. of *p/o* increases as the reaction progresses. The mol. amount of (**I**) rearranged exceeds the mol. equiv. of $AlCl_3$ employed if the amount of $AlCl_3$ is < the mol. proportions. $Al(OPh)Cl_2$ (**II**), the $AlCl_3$ salts of *o*- and *p*-$OH \cdot C_6H_4 \cdot CO \cdot C_7H_{15}$, and the $AlCl_3$ complex of octophenone cause the rearrangements of (**I**). Suggested mechanisms are: (**I**) + (**II**) → $OPh \cdot C(C_7H_{15}):O \cdot AlCl_2 \cdot OPh$ → $Al(OPh)_2Cl$ + $C_7H_{15} \cdot COCl$ → $C_7H_{15} \cdot CO \cdot C_6H_4 \cdot O \cdot AlCl \cdot OPh$ → HCl and (**I**) + $AlCl_2 \cdot O \cdot C_6H_4 \cdot CO \cdot C_7H_{15}$ → $OPh \cdot C(C_7H_{15}):O \cdot AlCl_2 \cdot O \cdot C_6H_4 \cdot CO \cdot C_7H_{15}$ → $OPh \cdot AlCl \cdot O \cdot C_6H_4 \cdot CO \cdot C_7H_{15}$ + $C_7H_{15} \cdot COCl$ → $(C_7H_{15} \cdot CO \cdot C_6H_4 \cdot O)_2AlCl$. When substantially > mol. proportions of $AlCl_3$ are employed, the ratio of the isomerides is essentially independent of the amount of (**I**) rearranged. p-*Octoylphenyl octoate*, m.p. 56·5—57·5° (obtained also from *p*-$OH \cdot C_6H_4 \cdot CO \cdot C_7H_{15}$ and boiling $C_7H_{15} \cdot COCl$), is identified as an intermediate when sufficient $AlCl_3$ is present to form the $AlCl_3$–$C_7H_{15} \cdot COCl$ complex. The suggested mechanism then is: $OPh \cdot C(C_7H_{15}):OAl_3$ + $AlCl_3$ → (**II**) + $C_7H_{15} \cdot COCl, AlCl_3$ (**III**), followed either by (**II**) + (**III**) → $AlCl_2 \cdot O \cdot C_6H_4 \cdot C(C_7H_{15}):O \cdot AlCl_3$ + HCl or (**I**) + (**III**) → $C_7H_{15} \cdot CO \cdot C_6H_4 \cdot O \cdot CO \cdot C_7H_{15}, AlCl_3$ (**IV**) + HCl and (**IV**) + (**II**) → $2C_7H_{15} \cdot CO \cdot C_6H_4 \cdot O \cdot AlCl_2$ + HCl. Temp. > 140° favour the formation of *o*-hydroxyoctophenone, into which the *p*-compound rearranges at 180°. H. W.

Biochemical hydrogenations. VII. Hydrogenation of unsaturated substances in the animal body. F. G. Fischer and H. J. Bielig (*Z. physiol. Chem.*, 1940, **266**, 73—98; cf. A., 1937, III, 392).—Various unsaturated substances were administered to rabbits either by stomach tube or intramuscularly and the metabolic products in the urine were examined. $CHPh:CH \cdot COMe$ gave mainly $Ph \cdot [CH_2]_2 \cdot CHMe \cdot OH$, $[\alpha]_D^{20}$ +6·60°, a little $CHPh:CH \cdot CHMe \cdot OH$, and a *diol*, probably $OH \cdot CHPh \cdot CH_2 \cdot CHMe \cdot OH$. $CHPh:CH \cdot COEt$ likewise gave $Ph \cdot [CH_2]_2 \cdot CHEt \cdot OH$, $[\alpha]_D^{18}$ +8·3°, but no unsaturated carbinol or $(OH)_2$-compound. A small amount of a saturated phenolic *ketone*, m.p. 86—87° (*phenylhydrazone*, m.p. 115—117°), probably *p*-$OH \cdot C_6H_4 \cdot [CH_2]_2 \cdot COEt$, was also produced. $COPh \cdot CH:CHMe$ (toxic) afforded only the unsaturated $OH \cdot CHPh \cdot CH:CHMe$. $Ph \cdot [CH:CH]_2 \cdot COMe$ yielded $CHPh:CH \cdot [CH_2]_2 \cdot CHMe \cdot OH$ and a *dihydroxyphenylhexene*, $[\alpha]_D^{20}$ +2·88°. The phenolic products contained a singly unsaturated *carbinol*, m.p. 103—104°, $[\alpha]_D^{18}$ +9·70°, and a ketone, m.p. 69—70° (*semicarbazone*, m.p. 169—170°). On fission by O_3 both these phenolic products afforded *p*-$OH \cdot C_6H_4 \cdot CHO$. The hydrogenation in these products occurs only at the double linking $\alpha\beta$ to the CO. Carvone (toxic) and β-ionone were also examined. In these compounds the CO is transformed into carbinol with one ethylenic linking saturated. The alcohols are dextrorotatory. With cinnamic alcohol and acid there was evidence of simple hydrogenation of the double linking. On the other hand with $CHPh:CEt \cdot CH_2 \cdot OH$ and $CHPh:CEt \cdot CHO$, $CHPh:CEt \cdot CO_2H$ was produced with no evidence of hydrogenation. Δ^2-*cyclo*-Hexenol (toxic) and $\Delta^{4:6}$-dihydro-2-methylbenzyl alcohol yielded no recognisable products. Geraniol intramuscularly gave rise to Hildebrandt acid (Kuhn and Livada, A., 1933, 1325) and the corresponding 1 : 5-H_2-acid. Farnesol and phytol afforded farnesic and phytic acid respectively. Citronellol gave a dibasic *acid*, $C_{10}H_{16}O_4$, m.p. 83—84°, $[\alpha]_D^{18}$ +8·44° in 2N-NaOH, which is probably partly racemised Hildebrandt acid, and *η-hydroxy-ββζ-dimethyl-*Δ^{ϵ}*-octenoic acid*, b.p. 132—135°/1 mm., $[\alpha]_D^{18}$ +2·07° in 2N-NaOH. J. H. B.

Isomeric mandelohydrazones of benzoin. (Miss) E. M. Luis and A. McKenzie (*J.C.S.*, 1941, 647—652).—(−)-Benzoin and (−)-*mandelohydrazide* (**I**), m.p. 152—153°, $[\alpha]_D^{16}$ −52·7° in MeOH, in aq. AcOH at room temp. for 5 days yield (−)-*benzoin* (−)-*mandelohydrazone* (**II**), m.p. 166—167° (decomp.), $[\alpha]_D^{14}$ −33°, or $[\alpha]_{4358}^{17}$ +36·3° in MeOH. (+)-Benzoin and (+)-*mandelohydrazide* (**III**), m.p. 152—153°, $[\alpha]_D^{16}$ +52·2° in MeOH, in aq. AcOH–NaOAc afford (+)-*benzoin* (+)-*mandelohydrazone* (**IV**), m.p. 166—167° (decomp.), $[\alpha]_D^{17}$ +32·8°, or $[\alpha]_{4358}^{17}$ −31·3° in MeOH. Similarly prepared, but with more difficulty, in aq. NaOAc–HCl–EtOH at 100° (bath) for ½ hr., are (−)-*benzoin* (+)-*mandelohydrazone* (**V**) (+EtOH), m.p. 111—124°, $[\alpha]_D^{17}$ +170° in MeOH, and (+)-*benzoin* (−)-*mandelohydrazone* (**VI**) (+EtOH), m.p. indefinite, $[\alpha]_D^{17}$ −171° in MeOH. (**II**) and N-HCl at 100° (bath) give benzoin, $[\alpha]_D$ −73·9°, showing marked racemisation. *r*-Benzoin (**VII**) is resolved by adding a solution in EtOH to (**III**) in 2N-HCl and heating at 100° (bath) for ½ hr., when (**IV**) separates and is decomposed by 0·3N-H_2SO_4 at 100° to give optically pure (+)-benzoin; (**V**) is also isolable. In some experiments where (**I**) is used as resolving agent, (**VI**) [gives optically pure (+)-benzoin] and (**II**) separate; resolution takes an irregular course, and theoretical aspects are discussed. (**VII**) and *r*-mandelohydrazide (**VIII**) in aq. AcOH at room temp. give r-*benzoin* r-*mandelohydrazone*, *α-form*, m.p. 183—184° (decomp.), dimorphous, also obtained by allowing equimol. amounts of (**II**) and (**IV**) in EtOH to evaporate at room temp.; (**V**) and (**VI**) yield the *β-form*, m.p. 156—157° (decomp.); (**VII**) and (**VIII**) in EtOH–AcOH (reflux) give a mixture of *α*- and *β*-forms. *dl*-Hydratropaldehyde and (**VIII**) in EtOH yield r-*hydratropaldehyde* r-*mandelohydrazone*, m.p. 138—139°; r-*hydratropaldehyde* (+)-*mandelohydrazone* has m.p. 150—152°, $[\alpha]_D^{20}$ +80·7° in MeOH ("partially racemic"), but attempts at resolution failed; r-*hydratropaldehyde* (−)-*mandelohydrazone* has m.p. 150—152°. A. T. P.

Keto-alcohols. II. Synthetic compounds with corticosterone-like activity. W. H. Linnell and I. M. Roushdi (*Quart J. Pharm.*, 1941, **14**, 270—280; cf. A., 1940, II, 119). —*p*-$OAc \cdot C_6H_4 \cdot COCl$ and CH_2N_2–Et_2O at −10° to 0°, then at room temp., afford the diazo-ketone, m.p. 109—110°, converted by 2N-H_2SO_4–dioxan at 40°, then KOH–EtOH at 100° (bath), into *p*-hydroxybenzoylcarbinol, m.p. 173—174° (2 : 4-*dinitrophenylhydrazone*, m.p. 231—233°). α-$C_{10}H_7 \cdot COCl$ similarly affords *α*-naphthoylcarbinol, b.p. 90—93°/4 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 175—176°). m-*Nitrophenylacetyl chloride*, m.p. 72—73°, and PhOMe–$AlCl_3$–CS_2 at room temp., then at 50—60°, afford 3′-*nitro*-4-*methoxydeoxybenzoin*, m.p. 85—86°, converted by Fe–aq. $FeCl_3$ at 100° (bath) into the 3′-NH_2-compound, m.p. 123—124° (hydrochloride, m.p. 164—166°), and thence (diazo-reaction) into the 3-CN-compound, m.p. 84—85°, and (HCl–AcOH) 4-*methoxydeoxybenzoin*-3′-*carboxylic acid* (**I**), m.p. 167—168°. (**I**) and EtI–EtOH–NaOEt yield, after hydrolysis with KOH–EtOH, 4-methoxy-α-ethyldeoxybenzoin-3′-carboxylic acid, m.p. 105—106°, converted by MgEtI–Et_2O at room temp. into 4-methoxy-αβ-diethylstilbene-3′-carboxylic acid (**II**), m.p. 45—50°; its Ag salt and EtOH–MeI give an unstable Me ester, converted by MgMeI at room temp., then under reflux, into 4-hydroxy-3′-acetyl-αβ-diethylstilbene (glassy), m.p. 80—110° (decomp.). (**II**) and MgI_2–Et_2O–C_6H_6 afford, after removal of solvent, a residue which when heated at 160° gives 4-*hydroxy-αβ-diethylstilbene*-3′-*carboxylic acid*, m.p. 160—161°. 4-Acetoxy-αβ-diethylstilbene-3′-carboxylic acid, through the chloride and CH_2N_2, yield a diazo-ketone, decomposed by 2N-H_2SO_4–dioxan to 4-hydroxy-3′-hydroxyacetyl-αβ-diethylstilbene (**III**), glassy solid, m.p. 65—67° (2 : 4-dinitrophenylhydrazone, m.p. 180—193°). *p*-Hydroxy-aceto- or -propio-phenone does not show activity similar to that of progesterone. (**III**) and benzoylcarbinol, m.p. 75—76° (from H_2O) or 85—86° (ligroin), show a biological activity qualitatively similar to that of deoxycorticosterone. A. T. P.

Preparation of αβ-unsaturated ketones and their reaction with phenylhydrazine. L. C. Raiford and L. K. Tanzer (*J. Org. Chem.*, 1941, **6**, 722—731).—Condensation of derivatives of *o*-$OH \cdot C_6H_4 \cdot CHO$ with COPhMe and its substitution products gives αβ-unsaturated ketone (**I**) which may add a further mol. of the initial ketone provided that it contains no substituent. This result is favoured by long keeping of the reaction mixture. In only one case could a stable phenyl-

hydrazone be isolated from (I) and NHPh·NH_2 in spite of apparently favourable conditions; in all other instances the product becomes rearranged to a substituted pyrazoline. The following *benzylidenediacetophenones* [*phenyldiphenacylmethanes*] are described in which the substituents are present in the CHPh residue: 5-*bromo*-2-*benzyloxy*-, m.p. 99·5—100°; 3 : 5-*dibromo*-2-*benzyloxy*-, m.p. 147—148°; 3 : 5-*dibromo*-2-*hydroxy*-, m.p. 120—121°; 3 : 5-*dibromo*-4-*hydroxy*-, m.p. 154—155°. The following *Ph styryl ketones* have been prepared, the substituents in the Ph and CH:CHPh residues being placed in this order: 4-*Me*-, 5-*Br*-2-*OH*-, m.p. 188° (decomp.), 4-*OMe*-, 5-*Br*-2-*OH*-, m.p. 174° (decomp.); 4-*Cl*-, 5-*Br*-2-*OH*-, m.p. 184° (decomp.); 4-*Br*-, 5-*Br*-2-*OH*-, m.p. 178—178·5° (decomp.); 4-*Me*-, 5-*Br*-2-*OMe*-, m.p. 130—131°; 4-*Me*-, 5-*Br*-2-*OEt*-, m.p. 144—145°; —, 5-*Br*-2-*O*·CH_2Bz-, m.p. 162—163°; 4-*Me*-, 5-*Br*-2-*O*·CH_2Bz-, m.p. 160—161°; 4-*OMe*-, 5-*Br*-2-*O*·CH_2Bz-, m.p. 156—158°; 4-*Cl*-, 5-*Br*-2-*O*·CH_2Bz-, m.p. 158—159°; —, 3 : 5-Br_2-2-*OH*-, m.p. 164—165°; 2-*Cl*-, 3 : 5-Br_2-2-*OH*-, m.p. 162—163°; 4-*Cl*-, 3 : 5-Br_2-2-*OH*-, m.p. 197—200° (decomp.); 4-*Br*-, 3 : 5-Br_2-2-*OH*-, m.p. 205—206° (decomp.); 4-*Me*-, 3 : 5-Br_2-2-*OH*-, m.p. 178—179° (decomp.); 4-*OH*-, 3 : 5-Br_2-2-*OH*-, m.p. 225—227° (decomp.); 4-*OMe*-, 3 : 5-Br_2-2-*OH*-, m.p. 189° (decomp.); 4-NH_2-, 3 : 5-Br_2-2-*OH*-, m.p. 195—196° (decomp.); 4-*Me*-, 3 : 5-Br_2-2-*OH*-, m.p. 136—137°; —, 3 : 5-Br_2-2-*O*·CH_2Ph-, m.p. 111—112°; 4-*Me*-, 3 : 5-Br_2-2-*O*·CH_2Ph-, m.p. 128—129°; 4-*OMe*-, 3 : 5-Br_2-2-*O*·CH_2Ph-, m.p. 137—137·5°; —, 3 : 5-Br_2-4-*OH*-, m.p. 160—161°; 4-*Me*-, 3 : 5-Br_2-4-*OH*-, m.p. 175—176°; 4-NH_2-, 3 : 5-Br_2-4-*OH*-, m.p. 227—228°; 2-*Cl*-, 3 : 5-Br_2-4-*OH*-, m.p. 187—188°. The following *distyryl ketones* are described, substituents being arranged in order as they are present in the first or second CH:CHPh residues: —, 5-*Br*-2-*OH*-, m.p. 179—180° (decomp.); —, 6-*Br*-3 : 4-O_2CH_2-, m.p. 147—148°; —, 3 : 5-Br_2-2-*OH*-, m.p. 160—160·5° (decomp.); 4-*Me*-, 3 : 5-Br_2-2-*OH*-, m.p. 181—182° (decomp.); 4-*OMe*-, 3 : 5-Br_2-2-*OH*-, m.p. 171—172° (decomp.); 4-NO_2-, 3 : 5-Br_2-2-*OH*-, m.p. 216—217° (decomp.); 4-*Ph*-, 3 : 5-Br_2-2-*OH*-, m.p. 188—189° (decomp.); 4-*Br*-, 3 : 5-Br_2-2-*OH*-, m.p. 193° (decomp.); 6-*Br*-3 : 4-O_2CH_2-, 3 : 5-Br_2-2-*OH*-, m.p. 200—201° (decomp.); 3 : 5-Br_2-4-*OH*-, 3 : 5-Br_2-2-*OH*-, m.p. 205—206° (decomp.); 5-*Br*-2-*O*·CH_2Ph-, 3 : 5-Br_2-2-*OH*-, m.p. 186—187° (decomp.); 3 : 5-Br_2-2-*OMe*-, 3 : 5-Br_2-2-*OH*-, m.p. 202—203° (decomp.); 3 : 5-Br_2-2-*O*·CH_2Ph-, 3 : 5-Br_2-2-*OH*-, m.p. 200—201° (decomp.); 3 : 5-Br_2-4-*OH*-, 3 : 5-Br_2-4-*OH*-, m.p. >275°. The following substitution products of 1-phenylpyrazoline have been prepared; the substituents are placed in order as they are present in substituted Ph or CH:CHPh at $C_{(3)}$ or substituted Ph at $C_{(5)}$: 4-*OMe*-, 5-*Br*-2-*O*·CH_2Ph-, m.p. 82°; 4-*Br*-, 3 : 5-Br_2-2-*OH*-, m.p. 175—177°; 4-*Br*-, 3 : 5-Br_2-4-*OH*-, m.p. 189—190°; 4-*Me*-, 3 : 5-Br_2-2-*O*·CH_2Ph-, m.p. 183—184°; 4-*OMe*-, 3 : 5-Br_2-2-*OH*-, m.p. 193—194°; 3 : 5-$C_6H_3Br_2$·*CH*:*CH*-2-*OH*-, 4-*Br*-, m.p. 238—239°; 3 : 5-$C_6H_3Br_2$·*CH*:*CH*-2-*OH*-, 3 : 5-Br_2-2-*O*·CH_2Ph, m.p. 145—155°. H. W.

Michael condensation. VII. Activation of the methylene group by carbon–carbon unsaturation. R. S. Taylor and R. Connor (*J. Org. Chem.*, 1941, **6**, 696—704).—CH_2 is reactive in the Michael condensation when it is activated by two C:C double linkings which may be part of aromatic systems, conjugated olefinic linkings, or non-aromatic and non-conjugated. In the presence of 1 equiv. of NaOEt fluorene (**I**) reacts (2—27%) with CHPh:CH·COPh, CHPh:CH·CO·C_6H_4Br-*p*, and CHPh:CHAc to give *β-phenyl-β*-9-*fluorenyl-propiophenone*, m.p. 127—128° (corr.), -p-*bromopropiophenone*, m.p. 159—160° (corr.), and a termol. product, (?) *ε-acetyl-δζ-diphenyl-ζ*-9-*fluorenylhexan-β-one*, m.p. 250° (decomp.), respectively. Since condensation does not occur with piperidine (**II**) or ⅛ equiv. of NaOEt, (**I**) must be considered as a relatively weak addendum. 2 : 7-Dibromofluorene (**III**) behaves similarly but is somewhat more reactive (11—48% of adducts), giving *β-phenyl-β*-2 : 7-*dibromo*-9-*fluorenyl-propiophenone*, m.p. 184—185° (corr.), -p-*bromopropiophenone*, m.p. 170—171° (corr.), [with (?) α-(*β*-p-*bromobenzoyl-α-phenylethyl*)-*β-phenyl-β*-2 : 7-*dibromo*-9-*fluorenyl*-p-*bromopropiophenone*, m.p. 255° (decomp.)], and *δ-phenyl*-δ-2 : 7-*dibromo*-9-*fluorenylbutan-β-one*, m.p. 159—160° (corr.), respectively. Even in the presence of 1 equiv. of NaOEt, (**I**) and (**III**) do not react with *αβ*-unsaturated esters or with *m*- or *p*-NO_2·C_6H_4·CH:CH·COPh. *cyclo*Pentadiene (**IV**) is a highly active compound since it reacts with *αβ*-unsaturated ketones in presence of (**II**). Whilst some addition occurs in boiling C_6H_6, better yields (25—30%) are obtained by carrying out the change under pressure to prevent loss of (**IV**); *β-cyclo*pentadienyl-*β*-phenylpropiophenone [*oxime*, m.p. 165·5—166·5° (corr.)] and -p-*bromopropiophenone* (**V**), m.p. 107—108°, are described. Attempts to condense (**IV**) with unsaturated ketones in presence of NaOEt give dark red tars probably because of fulvene formation. The Na compound of (**IV**), obtained by use of $NaNH_2$ in liquid NH_3, gives tars with CHPh:CH·COPh but also 1-*ββδ-dibenzoyl-αγ-diphenyl*-n-*butyl*-$\Delta^{2:4}$-*cyclopentadiene*, m.p. 260° (decomp.). The structure of (**V**) is established by its hydrogenation (Pd–PdO_2 in anhyd. Et_2O) to 1-p-*β*-cyclo*pentyl-β-phenyl*-p-*bromopropiophenone* (**VI**), m.p. 109—110° (corr.), also formed together with some *αγ-di*cyclo*pentyl-γ-phenyl-α*-p-*bromophenylpropan-α-ol*, m.p. 165—166°, from Mg *cyclo*pentyl bromide and CHPh:CH·CO·C_6H_4Br (**VII**). $\Delta^{\alpha\delta}$-Pentadiene and (**VII**) in presence of 1 equiv. of NaOEt afford *β-phenyl-γ-vinyl*-Δ^{δ}-*penienyl* p-*bromophenyl ketone*, m.p. 107—108° (corr.), also obtained with α-(p-*bromophenacylphenylmethyl*)-*β*-γ′-$\Delta^{\alpha'\delta'}$-*pentadienyl-β-phenylethyl* p-*bromophenyl ketone*, m.p. 225° (decomp.), from the Na derivative of (**VIII**) of (**VII**) obtained by using Na in liquid NH_3. The absence of any shift of the double linking of (**VII**) during the production of (**VIII**) is established by treating (**VIII**) with CO_2, hydrogenating the acid, and converting it into $CHEt_2$·CO·NH_2, m.p. 106—107° (corr.). H. W.

Michael condensation. VI. Instability of some additive products. P. L. de Benneville, D. D. Clagett, and R. Connor (*J. Org. Chem.*, 1941, **6**, 690—695).—In some cases additive products which might be expected from the Michael condensation are so readily cleaved that they cannot be isolated in the presence of NaOEt; such failure cannot be attributed solely to steric hindrance. Alkylation is attempted by treatment of the compound under investigation with NaOEt and alkyl halide in EtOH for 42 hr. (*a*) at the b.p. of the mixture or for 3 weeks at room temp. (*b*). Methylation of CH_2Bz·CHPh·$CH(CO_2Et)_2$ (**I**) by (*a*) or (*b*) gives CH_2Bz·CHPh·$CMe(CO_2Et)_2$ (**II**) with ~25% cleavage to $CHMe(CO_2Et)_2$ and CHPh:CH·COPh (**III**); with EtI and CH_2PhCl only cleavage products result, reaction with EtI probably being: $CH_2(CO_2Et)_2$ + (**III**) ⇌ (**I**) → CH_2Bz·CHPh·$CEt(CO_2Et)_2$ (**IV**) ⇌ (**III**) + $CHEt(CO_2Et)_2$. The difference between the results of methylation and ethylation of (**I**) probably depends on the relative rates of alkylation and retrogression. Methylation occurs rapidly enough to remove the alkoxide before (**II**) undergoes complete retrogression although (**II**) is almost completely cleaved with 1 equiv. of catalyst. Ethylation does not occur sufficiently rapidly to allow (**IV**) to be isolated. Retrogression occurs over a wide temp. range since additive products could not be isolated from (**III**), $CHEt(CH_2Et)_2$, CHPhEt·CO_2Et, or $CHPh(CO_2Et)_2$ at −78°. (**I**) and CHPh·CO_2Et (method *b*) give 51% of CH_2Bz·$[CHPh]_2$·CO_2Et (**V**), which is almost completely unchanged by NaOEt and $CH_2(CO_2Et)_2$. (**V**) (41·7%) is obtained from (**III**), $CH_2(CO_2Et)_2$, and CHPh·CO_2Et. H. W.

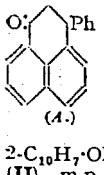
1-Keto-2-phenyl-1 : 2 : 3 : 4-tetrahydronaphthalene. A. A. Plentl and M. T. Bogert (*J. Amer. Chem. Soc.*, 1941, **63**, 2534—2535).—Priority in the prep. of this substance is acknowledged (cf. A., 1941, II, 190; Newman, A., 1939, II, 55; Crawford, A., 1939, II, 206). Its semicarbazone has m.p. 254° after sintering and decomp. R. S. C.

Optical isomerides of *cis*-1-keto-9-methyldecahydronaphthalene. A. A. Plentl and M. T. Bogert (*J. Org. Chem.*, 1941, **6**, 669—683).—Dropwise addition of 2-methyl-Δ^1-*cyclo*hexenylacetic acid, b.p. 137—139°/10 mm. (Chuang *et al.*, A., 1936, 988), to $SOCl_2$ gives the *chloride*, b.p. 86—89°/10 mm., transformed by CH_2N_2 in abs. Et_2O at 0° into the non-cryst. diazoketone, which is unstable to light and heat. It is converted by aq. NH_3 and $AgNO_3$ in dioxan at 100° into *β*-2-*methyl*-Δ^1-cyclo*hexenylpropionamide*, m.p. 135°, by Ag_2O and boiling EtOH into *Et β*-2-*methyl*-Δ^1-cyclo*hexenylpropionate*, b.p. 95—97°/10 mm., and by $Na_2S_2O_3$ and Ag_2O in aq. dioxan into *β*-2-*methyl*-Δ^1-cyclo*hexenylpropionic acid* (**I**), b.p. 112—113°/14 mm. From the viewpoint of overall yield the indirect methods have no advantage over the direct process. $SOCl_2$ and (**I**) in anhyd. C_5H_5N–Et_2O at 0° give the chloride and thence the diazo-ketone, which is smoothly converted into γ-2-methyl-Δ^1-*cyclo*hexenylbutyric acid (**II**), b.p. 166—167°/10 mm., m.p. 43° (*Et* ester, b.p. 77—78°/0·5 mm.). Cyclisation

of (II) is achieved by the method of Cook *et al.* (A., 1936, 74) without isolation of the intermediate Cl-ketone (which could not be distilled without decomp. at 0·1 mm. and is therefore immediately heated with $NPhMe_2$ at 180°), thereby yielding a mixture of 1-*keto*-9-*methyloctahydronaphthalenes*, (i) an unsaturated, camphoraceous liquid (**III**), b.p. 66—67°/0·5 mm. (*semicarbazone*, m.p. 228—229°; *oxime*, m.p. 105°), which polymerises to a yellow resin when kept, and (ii) a colourless liquid (**IV**), b.p. 70—71°/0·5 mm. (*semicarbazone*, m.p. 168°; *oxime*, m.p. 120°), in which the position of the double linking in the individuals could not be established. Oxidation (NaOBr in C_5H_5N) of (**IV**) gives only resinous material and cryst. products are not obtained from it when treated with BuO·NO, glacial AcOH, and conc. HNO_3. The unsaturated oximes are reduced (H_2–PtO_2–AcOH) to *cis*-9-methyl-1-decahydronaphthylamine *A* (*hydrochloride*; *Bz* derivative, m.p. 142°). (**III**) or (**IV**) is similarly hydrogenated to cis-9-*methyl*-1-*decahydronaphthol*, b.p. 95°/1 mm. (3 : 5-*dinitrobenzoate*, m.p. 126°), which is oxidised (CrO_3 in AcOH) to *cis*-1-keto-9-methyldecahydronaphthalene, b.p. 58·5°/0·7 mm. [*semicarbazone*, m.p. 225°; *oximes*, m.p. 106° (**V**) and 88° (**VI**)], which can also be obtained by cautious hydrogenation (PtO_2 in AcOH) of the mixture of unsaturated ketones. Na and EtOH reduce (**V**) and (**VI**) to cis-*β-methyl*-1-*decahydronaphthylamine* B (**VII**), b.p. 65—68°/1 mm. (*hydrochloride*; *Bz* derivative, m.p. 158—159°), which rapidly absorbs CO_2 from the atm. Crystallisation of the α-bromo-π-camphorsulphonates of (**VII**) from abs. EtOH affords two *salts*, one of which, $[\alpha]_D$ +68·8° in H_2O, gives (+)-*cis*-9-methyl-1-decahydronaphthylamine-*B* hydrochloride, $[\alpha]_D$ +7·0° in H_2O, and the other, $[\alpha]_D$ +59·2° in H_2O, yields the (−)-amine hydrochloride, $[\alpha]_D$ −6·9° in H_2O. Treatment of the (+)-amine with $NaNO_2$ and AcOH gives a mixture of hydrocarbon, alcohol, and ester which is hydrolysed; the neutral portions are oxidised to (+)-*cis*-1-keto-9-methyldecahydronaphthalene, b.p. ~60°/1 mm., $[\alpha]_D$ +4·2° in EtOH (semicarbazone, m.p. 228°, $[\alpha]_D$ + 1·1° in EtOH). Similarly the (−)-amine affords (−)-*cis*-1-keto-9-methyldecahydronaphthalene, b.p. 60°/1 mm., $[\alpha]_D$ −3·9° in EtOH (semicarbazone, m.p. 228°, $[\alpha]_D$ −0·90° in EtOH). H. W.

New route to the synthesis of dibenzfluorenones. G. Swain and A. R. Todd (*J.C.S.*, 1941, 674—679).—β-$C_{10}H_7$·NAc·NO (**I**) and β-$C_{10}H_7$·$CO_2C_5H_{11}$ (mainly *iso*-) (**II**) at 27—29°, then at room temp., yield a mixture of esters, hydrolysed by KOH–EtOH to 1 : 2′-*dinaphthyl*-2-, m.p. 204—205°, and -3(or 6 or 7)-*carboxylic acid*, m.p. 231—232°, and the former acid or the crude mixture with H_2SO_4–AcOH at 100° (bath) gives 1 : 2 : 5 : 6-dibenzfluorenone, m.p. 164—165°; aq. N_2H_4 at 200° then affords 1 : 2 : 5 : 6-dibenzfluorene. α-$C_{10}H_7$·$CO_2C_5H_{11}$ and (**I**) give a mixture, converted as above into 1 : 2 : 7 : 8-dibenzfluorenone, m.p. 265—266°, in poor yield, a *product* (? mixture), m.p. 182—183°, and 1 : 2′-*dinaphthyl*-4(or 5 or 8)-*carboxylic acid*, m.p. 206—207°. α-$C_{10}H_7$·NAc·NO and (**II**) afford much azo-compound, and subsequent treatment gives a little 3 : 4 : 5 : 6-dibenzfluorenone, m.p. 222—223°, together with some 1 : 2 : 8 : 9-dibenz-10-anthrone, m.p. 186—187°. A. T. P.

***peri*Naphthene series. IV. Attempts to synthesise 9-phenyl*peri*naphthan-7-one.** C. F. Koelsch and J. A. Anthes (*J. Org. Chem.*, 1941, **6**, 558—565; cf. A., 1938, II, 19; 1939, II, 118).—The constitution assigned previously to 1-methoxy-9-phenyl*peri*naphthanone is confirmed by the isolation of a :*CHPh* derivative, m.p. 168—170°. The following syntheses did not lead to the parent ketone (*A*). 1-$C_{10}H_7$·COMe, PhCHO, and NaOH in aq. EtOH afford 1-cinnamoylnaphthalene, converted by $AlCl_3$ in boiling CS_2 into *peri*naphthen-7-one (**I**), m.p. 153·5—154°, also obtained by successive treatments of CHPh:CH·CO_2H and $C_{10}H_8$ in C_6H_6 with PCl_5 and $AlCl_3$. Similar treatments of 2-$C_{10}H_7$·OMe lead to 2-methoxy-1-cinnamoylnaphthalene (**II**), m.p. 140—141°, obtained more tediously from 2 : 1-OMe·$C_{10}H_6$·COMe and PhCHO, and converted by $AlCl_3$ in CS_2 at room temp. into 5 : 6-*benzoflavanone*, m.p. 116—117° (:*CHPh* derivative, m.p. 164—166°). $AlCl_3$ and (**II**) in boiling C_6H_6 afford 6-*hydroxy*per*inaphthen*-7-*one*, m.p. 200—201°, which could not be methylated by using the Na salt and Me_2SO_4, the Ag salt and MeI, or MeOH–HCl and could not be acetylated or benzoylated. With aq. $KMnO_4$ in alkaline and subsequently in acid solution it yields K H_2 hemimellitate.



(*A*.)

1-*Phenyl*per*inaphthenone*, m.p. 150—152°, is formed when (**I**) and excess of MgPhBr are boiled in Et_2O and the alkali-sol. oily product is distilled under reduced pressure; it is oxidised ($KMnO_4$) to 2 : 1 : 8-$C_{10}H_5Ph(CO)_2O$. 1-$C_{10}H_7$·COPh, CH_2Br·CO_2Et, and granular Zn in boiling C_6H_6 afford *Et β-hydroxy-β-phenyl-β*-1-*naphthylpropionate*, m.p. 116·5—118°, which in conc. H_2SO_4 at room temp. yields 9-phenyl*peri*naphthen-7-one (**III**), m.p. 142—143°. (**III**) is reduced by Zn dust and AcOH to 7 : 7′-*di*-(6-*hydroxy*-4-*phenyl*per*inaphthenyl*) (**IV**), m.p. 127—128° to a dark red liquid after softening at 124°, and 6-hydroxy-4-phenyl*peri*naphthene (**V**), m.p. 136—138°. (**V**) and O_2 readily yield (**IV**) and then (**III**) but re-conversion into (**III**) is not quant. (**III**) and (**V**) in ligroin give the equiv. amount of (**IV**). At the dropping Hg cathode two potentials are observed in the reduction of (**III**) corresponding with the two stages of the process. H. W.

Reactions and enolisation of cyclic diketones. V. (1) Carbonyl reactions. C. F. Koelsch and C. D. Le Claire (*J. Org. Chem.*, 1941, **6**, 516—533).—The mutual activating effect of the CO groups in some derivatives of indane-1 : 2-dione is > that in acyclic α-diketones. Although the 1-CO is more available for reaction, the 2-CO is more polar. Polarisation of the 2-CO is diminished when aromatic nuclei are substituted on $C_{(3)}$. Mesityl oxide and $AlCl_3$ in C_6H_6 at 10° afford δ-phenyl-δ-methylpentan-β-one, b.p. 115°/11 mm., oxidised by NaOCl to $CPhMe_2$·CH_2·CO_2H, m.p. 58—59°, which is converted by successive treatments with PCl_5 and $AlCl_3$ into 3 : 3-dimethylindan-1-one (**I**), b.p. 110°/8 mm. (**I**), BuO·NO, and NaOMe in MeOH at 0° afford 2-*oximino*-3 : 3-*dimethylindan*-1-*one* (**II**), white scales from H_2O, m.p. 138—141°, or white hexagonal plates from EtOH, m.p. 145—147° (benzoate, m.p. 169—171°), which is hydrolysed by 40% CH_2O and conc. HCl in boiling AcOH to 3 : 3-*dimethylindane*-1 : 2-*dione* (**III**), m.p. 106—107°. This give colourless additive *products*, $C_{11}H_{11}O_5SNa$ and $C_{11}H_{10}O_2$,KCN,H_2O, with $NaHSO_3$ and aq. KCN, respectively. According to conditions (**III**) gives the lower-melting variety of (**II**) or the *dioxime*, m.p. 191—193° (decomp.) (*dibenzoate*, m.p. 192—193°), also obtained by the (slow) oximation of (**II**). *o*-$C_6H_4(NH_2)_2$ and (**III**) in hot EtOH rapidly give the *quinoxaline* derivative, $C_{17}H_{14}N_2$, m.p. 146°. Dimethylhomophthalic anhydride, m.p. 81—82°, is formed when (**III**) is oxidised by H_2O_2 containing a little NaOH in EtOH and the product is heated. (**III**) is converted by MeOH nearly saturated with HCl into 2 : 2-*dimethoxy*-3 : 3-*dimethylindan*-1-*one*, m.p. 75—76°, which with MgPhBr in Et_2O at 35° gives a non-cryst. product, converted by boiling NaOH–MeOH into (δ) α-o-α-hydroxybenzylphenyl*iso*butyric acid (**IV**) and 1-*phenyl*-3 : 3-*dimethylindan*-1-*ol*-2-*one* (**V**), m.p. 128—129°. (**V**) is also obtained from (**III**) and 1 equiv. of MgPhBr and is partly converted by boiling 25% KOH–aq. EtOH into (**IV**) [corresponding *lactone* (**VI**), m.p. 126—127°]. Oxidation (CrO_3 in AcOH at 100°) of (**VI**) yields α-o-*benzoylphenyl*isobutyric *acid*, m.p. 196—198° after softening at 188°, also obtained by oxidation of 3-phenyl-1 : 1-dimethylindene. With an excess of MgPhBr (**III**) gives 1 : 2-*diphenyl*-3 : 3-*dimethylindane*-1 : 2-*diol*, (**VII**), m.p. 125—126°, oxidised by $Pb(OAc)_4$ in C_6H_6 to o-α-*dibenzoylcumene*, m.p. 115—116°. Warm AcOH containing a little H_2SO_4 converts (**VII**) into a *ketone* (**VIII**), $C_{23}H_{20}O$, m.p. 125—126°, stable to KOH–EtOH but transformed by NaOH–KOH at 300° into an *acid*, $C_{23}H_{22}O_2$, m.p. 185—186°, which is stable towards $Cu(OAc)_2$ in boiling quinoline and loses NaOH when the Na salt is distilled with NaOH–CaO with re-formation of (**VIII**). Insolation of (**III**) in MeOH, EtOH, or $Pr^{\beta}OH$ causes oxidation of the alcohol and formation of (probably) 3 : 3-*dimethylindan*-2-*ol*-1-*one* (**IX**), m.p. 111—115° to an orange liquid. (**IX**) is almost quantitatively converted by $KMnO_4$ into (**III**). At its m.p. (**IX**) suffers disproportionation without evolution of gas into (**III**) and a pale yellow oil, transformed by BzCl into 1 : 2-*dibenzoyloxy*-3 : 3-*dimethylindane*, m.p. 86—87°. (**I**) is nitrated by HNO_3 (*d* 1·5) at −10° to 15° in presence of $CO(NH_2)_2$ to 6-*nitro*-3 : 3-*dimethylindan*-1-*one* (**X**), m.p. 133—134°, oxidised by $KMnO_4$ to nitrodimethylhomophthalic acid in good yield. (**X**) in Et_2O is converted by BuO·NO and AcCl into 6-*nitro*-2-*oximino*-3 : 3-*dimethylindan*-1-*one*, m.p. 210—222°, hydrolysed by AcOH, CH_2O, and conc. HCl to 6-*nitro*-3 : 3-*dimethylindane*-1 : 2-*dione* (**XI**), m.p. 172—174° (impure *dioxime*, m.p. 171—180°), which gives yellow solutions in alcohols and pink solutions in non-polar solvents. With a slight excess of 3% alkaline H_2O_2, (**XI**) gives 5-nitro-αα-dimethylhomophthalic acid (corresponding *anhydride*, m.p.

163—165°). With *o*-$C_6H_4(NH_2)_2$, (**VI**) gives the *quinoxaline* derivative, $C_{17}H_{13}O_2N_3$, m.p. 269—271°. 2-Oximino-3 : 3-diphenylindan-1-one, m.p. 206—209° (lit. 220°), is slowly hydrolysed by boiling AcOH–40% CH_2O–conc. HCl to 3 : 3-*diphenylindane*-1 : 2-*dione* (**XII**), m.p. 150—151° (*quinoxaline* derivative, m.p. 244—245°; 1-*oxime*, m.p. 215—217°), oxidised by 3% H_2O_2 to diphenylhomophthalic acid (*anhydride*, m.p. 227—228°). A large excess of MgIPhBr converts (**XII**) into a glassy solid, transformed by boiling AcOH containing a little conc. H_2SO_4 into 2 : 2 : 3 : 3-*tetraphenylindan*-1-*one*, (**XIII**), m.p. 185—186°. In xylene at 100° MgPhBr and 1 : 3 : 3-triphenylindan-1-ol-2-one afford 1 : 2 : 3 : 3-*tetraphenylindane*-1 : 2-*diol*, m.p. 177—178°, in good yield. This is converted by boiling AcOH containing a little conc. H_2SO_4 into (**XIII**) and 1 : 1 : 3 : 3-*tetraphenylindan*-2-*one*, m.p. 218—219°. H. W.

Reactions and enolisation of cyclic diketones. VI. 2 : 4 : 5-Triphenyl-Δ⁴-*cyclo*pentene-1 : 3-dione and 2 : 4 : 5-triphenyl-*cyclo*pentane-1 : 3-dione. C. F. Koelsch and S. Wawzonek (*J. Org. Chem.*, 1941, **6**, 684—689).—The marked tendency towards enolisation of 1 : 3-diketo*cyclo*pentane derivatives is almost completely absent from 1 : 3-diketo*cyclo*pentene compounds. Since similar observations have been made with 1 : 2-$(CO)_2$-compounds it appears that there is a tendency for one double linking to enter a 5-membered ring and a resistance to the entry of a second double linking. Diphenylmaleic anhydride (**I**), m.p. 157—158°, is conveniently obtained by the interaction of $COPh{\cdot}CO_2K$ and $CH_2Ph{\cdot}CO_2H$ in boiling Ac_2O. Alkaline hydrolysis of $CN{\cdot}CPh{:}CPh{\cdot}CN$ (**II**) gives (**I**) in 75% yield but the yields of (**II**) from $CH_2Ph{\cdot}CN$, I, and NaOMe under varied conditions do not exceed 30%. (**I**), $CH_2Ph{\cdot}CO_2H$, KOAc, and NaOAc at 220—225° give benzylidenediphenylmaleide, converted by boiling NaOMe–MeOH into 2 : 4 : 5-triphenyl-Δ⁴-*cyclo*pentene-1 : 3-dione (**III**), m.p. 167—168°, shown by its yellow colour to be ketonic. (**III**) does not react with Br in $CHCl_3$ but can be brominated in AcOH containing a little HBr to 2-*bromo*-2 : 4 : 5-*triphenyl*-Δ⁴-cyclo*pentene*-1 : 3-*dione* (**IV**), m.p. 133—134°. (**III**) slowly yields an *oxime*, m.p. 223—226° (decomp.). NaOH–EtOH dissolves (**III**) forming a purple Na salt which gives the yellow diketone when acidified at low temp. $NaNO_2$ or CrO_3 converts (**III**) into a di*cyclo*pentyl compound. (**III**), BzCl, and 10% KOH–H_2O give the yellow 2-*benzoyl*-2 : 4 : 5-*triphenyl*-Δ⁴-cyclo*pentene*-1 : 3-*dione* (**V**), m.p. 175—176°, whereas (**III**), BzCl, and C_5H_5N yield (**V**) and red 3-*benzoyloxy*-2 : 4 : 5-*triphenyl*-Δ²·⁴-cyclo*pentadienone*, m.p. 180—180·5°. Alkylation of (**III**) with Me_2SO_4 and aq. EtOH–NaOH affords solely the yellow 2 : 4 : 5-*triphenyl*-2-*methyl*-Δ⁴-cyclo*pentene*-1 : 3-*dione*, m.p. 106—108°, which is unaffected by long boiling with HBr–AcOH or by NH_4OH and is cleaved by boiling KOH–EtOH to (?) *γ-keto-αβδ-triphenyl*-Δ$^{\alpha}$-*hexenoic acid*, m.p. 169—170·5°. (**III**) is immediately enolised when treated with MgPhBr and further reaction leads to only a small amount of 4-hydroxy-2 : 3 : 4 : 5-tetraphenyl-Δ²-*cyclo*pentenone, m.p. 196—198° (lit. 210°); the main product is 2 : 4 : 5-*triphenyl*cyclo*pentane*-1 : 3-*dione* (**VI**), m.p. 203—205°, best obtained by reducing (**III**) with Zn dust and alkali. (**VI**) is described by Allen *et al.* (A., 1937, II, 245) as *αβδ*-triphenyl-Δ$^{\gamma}$-pentenoic acid. (**V**) is colourless, readily sol. in aq. Na_2CO_3, and titratable in presence of phenolphthalein. It is immediately converted by Br in AcOH at room temp. into (**IV**). With BzCl and alkali (**VI**) yields the colourless 2 : 5-*dibenzoyloxy*-1 : 3 : 4-*triphenyl*cyclo*pentadiene*, m.p. 138—139°. H. W.

Derivatives of 1 : 2 : 3 : 4-tetrahydrobenzene. VII. Synthesis of fumigatin. W. Baker and H. Raistrick (*J.C.S.*, 1941, 670—672; cf. A., 1942, II, 10).—1 : 3 : 4 : 5-$C_6H_2Me(OMe)_3$ and AcCl–$AlCl_3$–Et_2O afford 3-*hydroxy*-4 : 5-*dimethoxy*-2-*acetyltoluene*, m.p. 92°, converted by 3% aq. H_2O_2–NaOH into 2 : 3-*dihydroxy*-4 : 5-*dimethoxytoluene*, m.p. 101° (*diacetate*, m.p. 108°), which is oxidised by aq. $FeCl_3$ (+ a little HCl) under C_6H_6–light petroleum at room temp. to fumigatin [3-hydroxy-4-methoxy-2 : 5-toluquinone], identical with the natural product (cf. A., 1938, II, 237). A. T. P.

Action of thiophenols on quinones. O. Dimroth, L. Kraft, and K. Aichinger (*Annalen*, 1940, **545**, 124—139).—The action of *p*-O:C_6H_4:O (**I**) (2 mols.) on PhSH (1 mol.) in MeOH at −10° followed by addition of H_2O to the product gives 2-phenylthiol-*p*-benzoquinone (**II**), m.p. 114° (whence, by $COMe_2$–$SnCl_2$, the -quinol, m.p. 88°), and *p*-$C_6H_4(OH)_2$. (**I**) and PhSH (3 : 2) in 99—100% AcOH at room temp. and then at 60° afford 2 : 5-diphenylthiol-*p*-benzoquinone (**III**), m.p. 256—258°; the corresponding quinol has m.p. 94° (lit. 103°). Oxidation of the by-products from (**III**) by $Pb(OAc)_4$ leads to triphenylthiol-*p*-benzoquinone (**IV**), m.p. 172°. In 60% AcOH but under otherwise similar conditions the main product is 2 : 6-diphenylthiol-*p*-benzoquinone (**V**), m.p. 206° (lit. 203—204°). In 99—100% AcOH at 80° the products are ~28%, 6%, ~16%, and 40% of (**III**), (**V**), (**IV**), and (**II**), respectively. (**III**) and (**V**) with (**IV**) and unchanged (**II**) in each case are formed from (**II**) and PhSH (2 : 1) in 99—100% and 60% AcOH, respectively. Analogous methods lead to the isolation of o-*nitrophenylthiol-quinol*, m.p. 203—204° (oxidised by $FeCl_3$ in AcOH to the -quinone, m.p. 129—130°), 2 : 5-*di*-o-*nitrophenylthiol-quinol*, m.p. 264—265°, and -*p*-benzoquinone, m.p. 231—232°. p′-*Nitrophenyl*-p-*benzoquinone*, m.p. 179—180°, from the reactants in somewhat diluted AcOH, is reduced ($SnCl_2$ and HCl in AcOH or $Na_2S_2O_4$) to the -*quinol*, m.p. 182°. 2 : 5-*Di*-p′-*nitrophenylthiol*-p-*benzoquinone*, m.p. 260—270° (decomp.), and -*quinol*, m.p. 246—247°, o′-*anisylthiol*-p-*benzoquinone*, m.p. 130—131°, and -quinol, m.p. 142° (softens at 138°), 2 : 5-*di*-o′-*anisylthiol*-p-*benzoquinone*, m.p. 245° (softens at 241°), and -quinol, m.p. 158° (softens at 156°), and 2 : 5-*di*-p′-*anisylthiol*-p-*benzoquinone*, m.p. 272—273°, and -*quinol*, m.p. 148—149°, are described. 10-Thiolcamphor, best obtained from camphorsulphonyl chloride, conc. HCl, and Zn dust in EtOH, yields d- and l-10-*camphorthiol*-p-*benzoquinone*, m.p. 131·5°, $[\alpha]_{6240}^{20}$ −12·93° and +12·93° in AcOH, respectively, reduced to the -*quinols*, m.p. 124·7—125°, $[\alpha]_{6240}^{20}$ +9·42° and −9·42° in AcOH, respectively. The following are described: 2-*phenylthiol*-1 : 4-*naphthaquinone*, m.p. 160° (softens at 158°), and -*naphthaquinol*, m.p. 142—143°, which eliminates PhSH when treated with Zn dust and AcOH; 2-o-nitrophenylthiol-1 : 4-naphthaquinone, m.p. 203·5°, and -*naphthaquinol*, m.p. 181° after softening at 178° when brought into bath at 175°; 2 : 3-di-o-nitrophenylthiol-1 : 4-naphthaquinone, m.p. 255—156°, and -*naphthaquinol*, m.p. 235·5° (decomp.); 4-o-nitrophenylthiol-1 : 2-naphthaquinone, m.p. 215—217°, and -1 : 2-*naphthaquinol*, m.p. 186—187°. Unless conditions are suitably chosen the addition of PhSH to quinizarinquinone (**VI**) is accompanied by dehydrogenation of PhSH owing to the high oxidation potential of (**VI**). 1 : 4-*Dihydroxy*-2-*phenylthiol*-9 : 10-*anthraquinone*, m.p. 205·5°, is obtained by slow addition of PhSH in AcOH to (**VI**) in AcOH at 50° and removal of the product after cooling the mixture to 40°. The spectrum of its boric ester in Ac_2O is very characteristic. (**VI**) loses PhSH when boiled with Zn dust and AcOH. 1 : 4-*Dihydroxy*-o-*nitrophenylthiol*-9 : 10-*anthraquinone*, m.p. 256—257°, loses the thiol group when reduced with Zn dust in AcOH, $SnCl_2$ in AcOH–HCl, or $Na_2S_2O_4$ in alkaline solution. 1 : 4 : 5-Trihydroxy-2(or 3)-o-*nitrophenylthiol*- and 1 : 2 : 5 : 8-*tetrahydroxy*-4(?)-o-*nitrophenylthiol-anthraquinone*, m.p. −290° (acetate, m.p. 231—232°), are described. H. W.

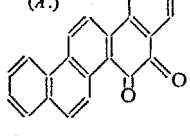
Biochemistry of micro-organisms. LXIX. Synthesis of catenarin (1 : 4 : 5 : 7-tetrahydroxy-2-methylanthraquinone), a metabolic product of species of *Helminthosporium*. W. K. Anslow and H. Raistrick (*Biochem. J.*, 1941, **35**, 1006—1010).—2-Hydroxy-4′ : 6′-dimethoxy-4-methylbenzophenone-4′-carboxylic acid [from 3 : 5 : 1 : 2-$(OMe)_2C_6H_2(CO)_2O$, *m*-cresol, and $AlCl_3$] and Br in AcOH give the 5-Br- (**I**), m.p. 260°, and 3 : 5-Br_2-derivative, m.p. 249° (decomp.). With conc. H_2SO_4–H_2BO_3, first at 100° and then at 150—160°, (**I**) gives 1 : 4 : 5 : 7-*tetrahydroxy*-2-*methylanthraquinone*, m.p. 246° (*tetra-acetate*, m.p. 235°), identical with national catenarin. F. R. S.

Structure of the so-called "toluidine-blue." C. F. H. Allen, G. F. Frame, and C. V. Wilson (*J. Org. Chem.*, 1941, **6**, 732—749).—Toluidine-blue (**I**) is the Na_2 salt of 1 : 5-di-2′-sulpho-4′-toluidino-4 : 8-dihydroxyanthraquinone whilst in toluidine-green (**II**) the groups are in the 1 : 4- and 5 : 8-positions respectively. (**I**), obtained by protracted extraction of the technical product with boiling abs. EtOH, gives a yellow vat on reduction of its aq. solution in presence of Raney Ni or by use of alkaline $Na_2S_2O_4$, from which it is regenerated by atm. oxidation. When heated with $ZnCl_2$, Zn dust, and NaCl at 230° and then at 260°, (**I**) affords some anthracene and 4 : 8-*di*-p-*toluidinoanthrarufin* (**III**), gradual decomp. >300°. "Oxidative hydrolysis" (dil. HNO_2; HCl with $FeCl_3$, KIO_4, $K_2S_2O_8$, or 30% H_2O_2) of (**I**) gives 1 : 4 : 5 : 8-tetrahydroxyanthraquinone (**IV**), visible softening without definite melting at ~350° [tetra-acetate, m.p. 281—282°

(decomp.) if brought into bath at 275° or decomp. 273—275° when moderately rapidly heated]. Addition of 3 : 6 : 1 : 2-$(OMe)_2C_6H_2(CO)_2O$ and quinol to NaCl–anhyd. $AlCl_3$ at 180° followed by heating of the mixture at 200—220° leads to (IV), also obtained from 5 : 8-dibromoquinizarin and aq. $Ca(OH)_2$ at 240—260°. " Reductive hydrolysis " (mossy Sn and HCl in MeOH) of (I) affords leuco-1 : 4 : 5 : 8-tetrahydroxyanthraquinone and 4 : 1 : 3-$NH_2{\cdot}C_6H_3Me{\cdot}SO_3H$ (V); alizarinviridin under these conditions passes into leucoquinalizarin and (V). SO_2Cl_2 converts finely-divided anthrarufin in $PhNO_2$ at 100° into 4 : 8-dichloroanthrarufin (VI), m.p. 336—337° (slight sublimation), whilst KNO_3 transforms a solution of it in conc. H_2SO_4 containing H_3BO_3 at 10—15° into 4 : 8-dinitroanthrarufin. (VI) is converted by a large excess of *p*-$C_6H_4Me{\cdot}NH_2$ at 160—175° into 4 : 8-di-*p*-toluidinoanthrarufin, sulphonated (conc. H_2SO_4 at 95—98°) and then transformed into the Na_2 salt, identical with (I). Isomeric *di*-m- and *di*-p-*toluidino*-dyes are derived from *m*- and *p*-$C_6H_4Me{\cdot}NH_2$ which resemble (I) in solubility and behaviour on heating. In conc. H_2SO_4 (I) gives a yellow-green colour whereas the *m*- and *o*-compounds give bluish-green and greenish-blue shades. Addition of an intimate mixture of 3 : 6 : 1 : 2-$C_6H_2Br_2(CO)_2O$ (VII) and quinol to anhyd. $AlCl_3$ and NaCl at 200—220° leads to 5 : 8-*dibromoquinizarin* (VIII), m.p. 245°, converted by heating with *p*-$C_6H_4Me{\cdot}NH_2$ in presence of NaOAc or H_2BO_3 or in boiling C_5H_5N into 5 : 8-*di*-p-*toluidinoquinizarin* (IX), m.p. 311°, similarly derived from 5 : 8-dichloroquinizarin; similar compounds are obtained by using *o*- or *m*-$C_6H_4Me{\cdot}NH_2$. Disulphonation of (IX) and conversion into its Na_2 salt gives (II). (VIII) is converted by $OH{\cdot}[CH_2]_2{\cdot}NH_2$ in boiling C_5H_5N into 5 : 8-β-hydroxyethylaminoquinizarin, m.p. 215—220° (with sublimation), oxidatively degraded (HNO_3 in 50% AcOH) to (IV) and converted by conc. H_2SO_4 at 50—60° into 1 : 4-di-β-sulphatoethylamino-5 : 8-dihydroxyanthraquinone, *o*-$C_6H_4(CO)_2O$, 60% oleum, Br, and a little I at ~60° afford (VII), the structure of which is confirmed by its use in the synthesis of (II) and by its failure to condense with quinol in presence of conc. H_2SO_4. When AcOH is removed as completely as possible at 100° from the filtrate from (VII) and the residue is dissolved in the min. amount of hot H_2O, 3 : 4 : 1 : 2-$C_6H_2Br_2(CO_2H)_2$, m.p. 197° (decomp.), is obtained. It condenses with quinol in NaCl–$AlCl_3$ to 5 : 6-*dibromoquinizarin*, m.p. 227°, and affords a *Me* ester, m.p. 79°. If the AcOH filtrate from (VII) is conc. nearly to dryness on the water-bath and the residue is crystallised from hot Ac_2O the product isolated is 4 : 5 : 1 : 2-$C_6H_2Br_2(CO)_2O$, m.p. 212—214° (6 : 7-*dibromoquinizarin*, m.p. 296—298°). H. W.

Structures of degradation products of picene. T. W. Cook (*J.C.S.*, 1941, 685—687).—" Picylene ketone " (Bamberger *et al.*, A., 1895, i, 292), purified chromatographically, is mainly 2′ : 1′-naphtha-1 : 2-fluorenone (I), m.p. 205·5—206·5° (corr.), which is converted by $N_2H_4.H_2O$ at 220—240° (sealed tube) into the -1 : 2-fluorene (cf. A., 1934, 882). Picenequinone must be regarded as essentially (*A*). (I) and KOH at 240—250° yield a mixture of acids, containing picenic acid (II), m.p. 207—209° (corr.) (cf. *loc. cit.*), which is derived from 2-phenylphenanthrene. Formation of $(2\text{-}C_{10}H_7)_2$ from (II) (*loc. cit.*) must be attributed to the presence of impurity. A. T. P.

(*A.*)



IV.—STEROLS AND STEROID SAPOGENINS.

Formation of the molecular compound of *allo*- and *epiallo*-cholesterol from $\Delta^{2:5}$-cholestadiene. J. C. Eck and E. W. Hollingsworth (*J. Amer. Chem. Soc.*, 1941, **63**, 2320—2322).—In HCl–$CHCl_3$ $\Delta^{4:6}$-cholestadiene gives the $\Delta^{3:5}$-diene (I), m.p. 78·5—79°, $[\alpha]_D^{21}$ −103·6° in CCl_4, and the mol. compound (II), m.p. 140—141°, $[\alpha]_D^{23}$ +85·6° in CCl_4, of *allo*- and *epiallo*-cholesterol. The same products are obtained by HCl–$CHCl_3$ from (I) or the $\Delta^{2:4}$-diene [(I) obtained only impure]. The structure of (II) is confirmed by dehydration to (I) by HCl–EtOH, and separation into its constituents by digitonin. The origin of the H_2O for hydration of the diene and other aspects of the reaction mechanism are discussed. R. S. C.

5 : 6-Dihydrostigmasterol. A. Mazur (*J. Amer. Chem. Soc.*, 1941, **63**, 2442—2444).—The sterol mixture obtained (A., 1941, II, 167) from *Spongilla lacustris* in 0·75% yield is separated by chromatography into (?) impure ergosterol and 5 : 6-*dihydrostigmasterol* (I), m.p. 136·5—137°, $[\alpha]_D$ −41·8° [*acetate* (II), m.p. 137°, $[\alpha]_D$ −47·6°; *benzoate*, m.p. 137·5°, $[\alpha]_D$ −17·1°; 3 : 5-*dinitrobenzoate*, m.p. 200°, $[\alpha]_D$ −18·3°]. The structure of (I) is proved by its failure to give a cryst. dibromide or αβ-unsaturated ketone, by hydrogenation of (II) in *cyclo*hexane (PtO_2; slow unless a little AcOH is present) or AcOH (fast) to (?) 5 : 6-dihydrostigmastanyl acetate and ozonisation of (II) in AcOH to give an aldehyde (? $CHEtPr^{\beta}{\cdot}CHO$) (2 : 4-*dinitrophenylhydrazone*, m.p. 109°, α 0). Clionasterol may be (I). [α] are in $CHCl_3$. R. S. C.

Coprositostanol, m.p. 126—127°, $[\alpha]_D$ +24·6°.—See A., 1941, III, 1039.

Steroids. V. Acetolysis of the stereoisomeric 5 : 6-oxides and preparation of the acetates of Δ^4-androstene-3 : 17-dion-6(α)-ol and 6(α)-hydroxy-11-deoxycorticosterone. M. Ehrenstein (*J. Org. Chem.*, 1941, **6**, 626—646).—The higher-melting oxide (I), m.p. 221—222·5°, $[\alpha]_D^{28}$ −10° in $COMe_2$ (instead of +10° recorded previously in error), obtained by treatment of dehydroisoandrosterone acetate with $KMnO_4$ in $COMe_2$ (A., 1940, II, 376) is almost quantitatively converted by AcOH into androstane-3(β) : 5 : 6-(*trans*)-triol-17-one 3 : 6-diacetate (II), m.p. 216·5—217°, showing that the acetolytic rupture of the oxide ring has resulted in the formation of OAc at $C_{(6)}$ and OH at $C_{(5)}$. Under similar conditions the lower-melting oxide (III) affords *androstane*-3(β) : 5 : 6-(trans)-*triol*-17-*one* 3 : 5-*diacetate* (IV), m.p. 202·5—204°, $[\alpha]_D^{28.1}$ +22·7° in $COMe_2$, proving that rupture of the oxide ring involves the introduction of OAc at $C_{(5)}$ and OH at $C_{(6)}$. In agreement, boiling Ac_2O transforms (IV) into *androstane*-3(β) : 5 : 6(trans)-*triol*-17-*one triacetate*, m.p. 185—186°, $[\alpha]_D^{26.1}$ −8·2° in $COMe_2$, also obtained by more vigorous acetylation (Ac_2O + HCl) of (II). To bring these results into line with the observation of Hattori on the fission of cholesterol oxide (A., 1940, II, 84) it is proposed to name (I) 5 : 6-(α)-oxido- and (III) 5 : 6-(β)-oxido-androstan-3-(β)-ol-17-one acetate, thus reversing the previous nomenclature. The main product of the action of BzO_2H on dehydro*iso*androsterone is 5 : 6(α)-oxidoandrostan-3(β)-ol-17-one, converted by suitable treatment with glacial AcOH into androstane-3(β) : 5 : 6-(*trans*)-triol-17-one 6-monoacetate (V), m.p. 276—277° (slight decomp.), $[\alpha]_D^{23.9}$ +23·6° in MeOH, and (II); the latter substance is formed from (V) and Ac_2O. (V) is oxidised (CrO_3) to androstane-5 : 6(*trans*)-diol-3 : 17-dione 6-monoacetate, m.p. 219—220·5°, $[\alpha]_D^{26.1}$ +44·6° in $COMe_2$, which can be dehydrated to Δ^4-*androsten*-6(α)-*ol*-3 : 17-*dione acetate*, m.p. 174—176°, $[\alpha]_D^{26.7}$ +153·5° in $COMe_2$. In the capon comb growth test this is one fifth as active as androsterone or Δ^4-androstene-3 : 17-dione. The main product of the action of BzO_2H on Δ^5-pregnene-3(β) : 21-diol-20-one 21-monoacetate [? 21-acetoxy-Δ^4-pregnene-3(β)-ol-20-one] is 5 : 6(α)-*oxidopregnane*-3(β) : 21-*diol*-20-*one* 21-*monoacetate*, m.p. 195—197°, $[\alpha]_D^{26.1}$ +15·6° in $COMe_2$, converted by boiling glacial AcOH into (mainly) *pregnane*-3(β) : 5 : 6-(trans) : 21-*tetraol*-20-*one* 6 : 21-*diacetate* (VI), m.p. ~118°, becoming transparent at 126°, $[\alpha]_D^{26.1}$ +16·7° in $COMe_2$, and the 3 : 6 : 21-*triacetate*, m.p. 176—177·5°, $[\alpha]_D^{26.1}$ +3·5° in $COMe_2$, also obtained from (VI), Ac_2O, and C_5H_5N. Oxidation (CrO_3) of (VI) affords *pregnane*-5 : 6-(trans) : 21-*triol*-3 : 20-*dione* 6 : 21-*diacetate*, m.p. 183·5—164·5°, $[\alpha]_D^{26.1}$ +21·5° in $COMe_2$, dehydrated to Δ^4-*pregnene*-6(α) : 21-*diol*-3 : 20-*dione diacetate* [6(α)-*hydroxy*-11-*deoxycorticosterone diacetate* (VII)], m.p. 84—88°, $[\alpha]_D^{27.2}$ +114·3° in $COMe_2$. (III) produces no diabetogenic action and has no influence on the work performance of adrenalectomised rats. The daily dosage required for the maintenance of life of such rats has not been established with certainty, but it is definitely less active than 11-deoxycorticosterone acetate in this respect. H. W.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Catalytic hydrogenation of cyclic compounds possessing a carbonyl group. I, II. T. I. Vechotko (*J. Gen. Chem. Russ.*, 1941, **11**, 99—102, 103—107).—I. *cyclo*Hexanone or fenchone in AcOH containing 5% of HCl is hydrogenated (Pt-black catalyst) to *cyclo*hexanol or fenchyl alcohol, together with their acetates. With camphor the reaction involves the stages camphor → borneol + *iso*borneol → bornyl + *iso*bornyl

chloride → camphene hydrochloride → camphene → camphane. Hydrogenation does not take place in absence of HCl.

II. The velocity of hydrogenation of certain substances rises in the order carvone < pulegone < menthone < carvomenthone. The products are in all cases alcohols and their acetates. R. T.

Association of camphor with phenol and cresols.—See A., 1942, I, 22.

Oil of *Artemisia tridentata* (American sage brush). C. R. Kinney, T. W. Jackson, L. E. De Mytt, and A. W. Harris (*J. Org. Chem.*, 1941, **6**, 612—625).—The oil is isolated by steam-distillation of sage brush flower shoots from Utah and purified by fractional distillation. The most volatile fractions contain H_2O and $CH_2{:}CMe{\cdot}CHO$, identified as the 2 : 4-dinitrophenylhydrazone; some AcOH is also present and there are indications of the presence of other aldehydes. A simple terpene is isolated from the fraction of b.p. 140—144°; the low b.p., *d*, *n*, $[\alpha]_D$, and positive colour test with Ac_2O and H_2SO_4 all indicate that it is α-thujene. It is readily hydrogenated to $C_{10}H_{18}$ which has b.p. and *n* of thujane but *d* and $[\alpha]_D$ are low. Probably the terpene belongs to the C_9 series. The presence of α-pinene in the oil is confirmed by the nitrosochloride, but in the fraction of b.p. 152—153° a third terpene is found (small amount) which does not give a nitrosochloride and is possibly β-pinene. The oil contains cineole, identified by the additive products with H_3PO_4 and m-$C_6H_4(OH)_2$; *d* and *n* indicate the presence of other components but no reactions could be obtained for limonene, dipentene, terpinolene, sylvestrene, or phellandrene. α-Terpinene is identified. The fraction of b.p. >193° contains much *d*-camphor and an alcohol, *artemisol* (I), $C_{10}H_{18}O$, which is probably the substance peculiar to sage oil. When heated with MgMeI 1 mol. of (I) evolves 2 CH_4; this is ascribed to loss of H_2O from (I) since it contains only 1 O. This loss of H_2O is also observed under the influence of PhNCO, when the main product is $CO(NHPh)_2$. (I) is unsaturated and readily absorbs 1 H_2 (Adams), showing the presence of a double linking. With P_2S_5 followed by Na (I) affords *p*-cymene. Dihydroartemisol readily loses 1 H_2O to PhNCO; when dehydrated by fused $NaHSO_4$, heated over Na, and then oxidised it yields p-$C_6H_4(CO_2H)_2$, indicating a *p*-menthan-9-ol structure. (I) appears to be a *p*-menthenol in which the position of the double linking is undecided. H. W.

Synthesis of eudalene. N. N. Chaterjee and A. Bose (*J. Indian Chem. Soc.*, 1941, **18**, 196—200).—Et 6-methylcyclohexanone-2-carboxylate with Na, then $Cl{\cdot}[CH_2]_2{\cdot}CO_2Et$ in C_6H_6, or with NaOEt, $Cl{\cdot}[CH_2]_2{\cdot}CO_2Et$, and a trace of NaI in EtOH, or its Na salt with $Cl{\cdot}[CH_2]_2{\cdot}CO_2Et$ in EtOH, yields *Et*$_2$ 6-*methyl*cyclo*hexanone-2-carboxylate-2-propionate*, b.p. 158—165°/2·5 mm., hydrolysed (conc. HCl) to 6-*methyl*cyclo*hexanone-2-β-propionic acid*, m.p. 71°. The *Et* ester, b.p. 135°/3 mm., of this with Zn and $CH_2Br{\cdot}CO_2Et$ (trace of I) in C_6H_6 gives Et_2 6-methylcyclohexan-1-ol-, b.p. 167°/3 mm., dehydrated ($SOCl_2$–C_5H_5N–Et_2O) to *Et*$_2$ 6-*methyl*cyclo*hexylidene*-, b.p. 153°/3 mm., hydrogenated (PtO_2) to *Et*$_2$ 6-*methyl*-cyclo*hexane*-1-*acetate*-2-*propionate*, b.p. 149°/3 mm. Na in C_6H_6 converts this into *Et* 2-*keto*-8-*methyldecahydronaphthalene*-1- or -3-*carboxylate*, b.p. 150°/3 mm., hydrolysed and decarboxylated to 2-*keto*-8-*methyldecahydronaphthalene*, b.p. 101—104°/3 mm. (*semicarbazone*, m.p. 177°), which with $MgPr^{\beta}I$ yields eudalene. A. Li.

New synthesis of cadalene. P. C. Dutta (*J. Indian Chem. Soc.*, 1941, **18**, 233—237).—p-$C_6H_4Me{\cdot}COMe$ with NaOEt in light petroleum (b.p. 90—100°) gives p-*tolylmethylglycide Et ester*, b.p. 130—135°/5 mm., which with EtOH–NaOEt, then dil. HCl, gives p-$C_6H_4Me{\cdot}CHMe{\cdot}CHO$ (I). (I) with Zn and $CH_2Br{\cdot}CO_2Et$ yields *Et* γ-p-*tolyl*-β-*hydroxyvalerate*, b.p. 149°/5 mm., dehydrated ($SOCl_2$ in C_5H_5N) to *Et* γ-p-*tolyl*-Δ^{β}-*pentenoate*, b.p. 134—136°/6 mm., which rapidly polymerises on distillation. The lactone of the corresponding acid [from (I) and $CH_2(CO_2H)_2$ in C_5H_5N–piperidine] is reduced (P + HI) to p-$C_6H_4Me{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}CO_2H$, cyclised (85% H_2SO_4) to 1-*keto*-4 : 7-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 118°/4 mm. (*semicarbazone*, m.p. 195—196°), which with $MgPr^{\beta}I$ gives a mixture dehydrogenated (Se) to cadalene. A. Li.

Structure of gossypol. XXVI. Gossypolic acid. R. Adams, T. A. Geissman, W. R. Dial, and J. T. Fitzpatrick (*J. Amer. Chem. Soc.*, 1941, **63**, 2439—2441; cf. A., 1941, II, 142).—Ozonolysis of gossypol under various conditions gives ≯ small amounts of gossypolic acid [2 : 2′-dihydroxy-4 : 4′-di*isobutyryl*-6 : 6′-dimethyldiphenyl-3 : 3′-dicarboxylic acid], m.p. 241° (cf. Karrer *et al.*, A., 1932, 1256) (Me_2 ester Me_2 ether, m.p. 138—139°; Me_2 ether, new m.p. 231—233°), dehydrated by Cu powder in quinoline–N_2 at 180—185° to (?) 2 : 2′-*dihydroxy*-4 : 4′-*diisobutyryl*-6 : 6′-*dimethyldiphenyl* (15%), m.p. 252—253° (*Me_2 ether*, m.p. 125—127°). M.p. are corr. R. S. C.

VI.—HETEROCYCLIC.

Transformation of β-furfuraldoxime in tofuramide. A. Bryson and F. P. Dwyer (*J. Proc. Roy. Soc. New South Wales*, 1940, **74**, 471—474).—Furamide is produced from $H_2[Ni(C_5H_4O{\cdot}NO)_3]_2$ by keeping in $COMe_2$ for several weeks, by treating with $(CH_2{\cdot}NH_2)_2$ in C_6H_6, or (mixed with the oxime) by dissolving in hot C_5H_5N and pptg. with H_2O, or by keeping in C_6H_6, or in EtOH–NH_3 exposed to the air, from $Ni(C_5H_4O{\cdot}NO)_2$ and the oxime in C_6H_6 for 1 week, or from $[CuOH(C_5H_4O{\cdot}NO)_3]_2$ by boiling with the oxime in C_5H_5N or (+NaOAc) in $COMe_2$. These results are discussed in relation to the action of Raney Ni on aldoximes (Paul, A., 1937, II, 152, 323). A. Li.

Co-ordination compounds with furfuraldoxime as chelate group. III. Complex metallic derivatives of β(*anti*)-furfuraldoxime. A. Bryson and F. P. Dwyer (*J. Proc. Roy. Soc. New South Wales*, 1940, **74**, 455—470; cf. A., 1941, II, 199).—Na_2PdCl_4 in HCl with β-furfuraldoxime (I) yields *bisfurfuraldoximepalladous chloride* (II), $H_2[PdCl_2(C_5H_4O{\cdot}NO)_2]$ (*cis*- and *trans*-forms, interconverted by crystallising from $COMe_2$), which when boiled with NaOAc in MeOH–$COMe_2$ yields *bisfurfuraldoximepalladium* (III), converted by EtOH–HCl into (II). (III) with boiling C_5H_5N gives *bispyridinebisfurfuraldoximepalladium* (IV), which with dil. HCl yields (II), and with boiling MeOH or H_2O, (III). (III) with (I) (1 mol.) in boiling $CHCl_3$ affords monomeric *trisfurfuraldoximepalladium* (V) [sol. in aq. EtOH–NaOH, regenerated (with the dimeric form) on acidification], which yields with warm C_5H_5N, (IV), and with EtOH–HCl, (II). Na_2PdCl_6 with (I) (2 mols.) and excess of NaOAc gives a mixture of (V) and a *dimeride*, $H_2[(C_5H_4O{\cdot}NO)_2Pd(C_5H_4O{\cdot}NO)_2Pd(C_5H_4O{\cdot}NO)_2]$, which rapidly reverts to (V), and yields with C_5H_5N, (IV), with (I) (1 mol.), *tetrakisfurfuraldoximepalladium*, $H_2[Pd(C_5H_4O{\cdot}NO)_4]$, and with $(CH_2{\cdot}NH_2)_2$ in C_6H_6, *ethylenediaminebisfurfuraldoximepalladium* [the last two similarly obtained from (V)]. Methylation (MeI + NaOMe) of (V) yields (III) and *O*-methylfurfuraldoxime. K_2PtCl_4 with (I) (3 mols.) and NaOAc yields a mixture containing *trisfurfuraldoximeplatinum* (VI) and *bisfurfuraldoximeplatinous chloride* (VII), both sol. in aq. NaOH, repptd. by AcOH. (VII) is unaffected by contact with Zn in aq. $COMe_2$ for several days. With boiling $COMe_2$–MeOH–NaOAc (VII) slowly yields *bisfurfuraldoximeplatinum*, and with excess of (I) and NaOAc in boiling EtOH–$COMe_2$ gives *tetrakisfurfuraldoximeplatinum* [also obtained from (VI)] (sol. in aq. NaOH, repptd. by AcOH or NH_4Cl), which with warm C_5H_5N affords *bispyridinebisfurfuraldoximeplatinum*. Solutions of $Ni(OAc)_2$ with (I) and NaOAc or aq NH_3 yield dimeric *tris*- (VIII), converted by AcOH or by C_5H_5N followed by H_2O into *bis-furfuraldoximenickel*. (VIII) in C_6H_6 slowly gives an insol. *compound* of the same empirical formula, and yields with $(CH_2{\cdot}NH_2)_2$, *ethylenediaminebis*-, and with (I), *tetrakis-furfuraldoximenickel*, decomp. by NaOH. $Co(OAc)_2$ with (I) and aq. SO_2, then aq. NH_3, yields *bis*-, $Co(C_5H_4O{\cdot}NO)_2$, rapidly oxidised by air to *tris-furfuraldoximecobalt*, $Co(C_5H_4O{\cdot}NO)_3$ [also obtained from (I) and $Na_3Co(NO_2)_6$, $[CoCO_3(NH_3)_4]SO_4$, $[Co(NH_3)_4(H_2O)_2]Cl_2$, or $[Co(NH_3)_6]Cl_3$], which is unaffected by cold conc. HCl, and in C_6H_6 slowly deposits (?) an isomeride. $CuCl_2$ in MeOH with (I) and MeOH–NaOAc yields a *compound* (IX), $[CuOH(C_5H_4O{\cdot}NO)]_2$ (? having a diol bridge), unaffected by conc. aq. NH_3 or $(CH_2{\cdot}NH_2)_2$. $[Cu(C_5H_4O{\cdot}NO)_2]Cl_2$ (*loc. cit.*) with EtOH–NaOAc gives a greenish-brown solution (? containing $Cu(C_5H_4O{\cdot}NO)_2$], which with H_2O or Et_2O yields (IX). A. Li.

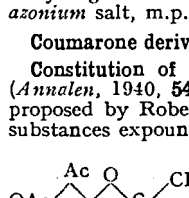
Lactones related to the cardiac aglycones. V. Synthesis of 5-alkyl-2-pyrones. J. Fried and R. C. Elderfield (*J. Org. Chem.*, 1941, **6**, 566—576).—Condensation of $Et_2C_2O_4$ with Et Δ^{α}-pentenoate by KOEt in EtOH–Et_2O yields *Et*$_2$ δ-*keto*-γ-*methyl*-Δ^{α}-*butene*-α*δ*-*dicarboxylate* (I) (at least two isomeric forms, one of which has m.p. 66—68° and gives a dark brown colour with $FeCl_3$); the 2 : 4-*dinitrophenylhydrazone* has m.p.

116—117°. (I) is hydrolysed by conc. HCl at 60—70° to the *acid*, m.p. 161—162° (p-*bromophenacyl* ester, m.p. 157—159°), which is converted by HBr–AcOH at 150° into 5-*methyl*-2-*pyrone*-6-*carboxylic acid* (II), m.p. 209—211° (*Me* ester, m.p. 130—131°); this is decarboxylated by distillation with Cu powder to 5-*methyl*-2-*pyrone*, m.p. 17—19°, which gives an additive *product*, m.p. 194·5—195·5° (decomp.), with maleic anhydride. (II) is converted by dry NH_4OAc in boiling AcOH–Ac_2O into 6-*hydroxy*-3-*methylpicolinic acid*, decomp. 290—300°, decarboxylated by distillation with Zn dust to 3-methylpyridine. Similarly $Et_2C_2O_4$ and Et Δ$^{\alpha}$-hexenoate are condensed to *Et*$_2$ δ-*keto*-γ-*ethyl*-Δ$^{\alpha}$-*butene*-αδ-*dicarboxylate*, two forms, m.p. 72—74° and 58—59°, respectively (either keto–enolic tautomerides or *cis–trans* isomerides), which gives a 2 : 4-*dinitrophenylhydrazone*, m.p. 102—105°. It is hydrolysed by conc. HCl to the *acid* (III), m.p. 116—119° (p-*bromophenacyl* ester, m.p. 115—116°), which gives a purple colour with aq. $FeCl_3$ and is converted by HBr–AcOH into 5-*ethyl*-2-*pyrone*-6-*carboxylic acid*, m.p. 158—159° (p-*bromophenacyl* ester, m.p. 113—114°), decarboxylated to 5-*ethyl*-2-*pyrone* (additive *compound*, m.p. 161—162°, with maleic anhydride). 2-Pyrone-6-carboxylic acid is similarly decarboxylated to 2-pyrone and converted by NH_4OAc in boiling AcOH into 2-pyridone-6-carboxylic acid, decomp. ~280°, converted by Zn dust into C_5H_5N. When heated in N_2 at 170—180° (III) evolves CO_2 and gives a yellow oil which yields a marked purple colour with $FeCl_3$ and a positive Tollens test. When exposed to air it deposits large, hygroscopic crystals, m.p. 100—104°, which do not give a colour with $FeCl_3$; the oil appears to contain γ-formyl-γ-ethylcrotonic acid. With Ac_2O it yields the *compound*, $C_9H_{12}O_4$, f.p. 15°. Mg *cyclo*hexylmethyl bromide and $CH(OEt)_3$ in dry Et_2O afford cyclo*hexylacetaldehyde Et*$_2$ *acetal*, b.p. 96—101°/11 mm., hydrolysed by boiling 5% HCl under N_2 to the aldehyde, b.p. 57—58°/10 mm. (*semicarbazone*, m.p. 158—159°; 2 : 4-*dinitrophenylhydrazone*, m.p. 124—125°). This condenses with $CH_2(CO_2H)_2$ in dry C_5H_5N at room temp. and then at 100° to γ-cyclo*hexylcrotonic acid*, m.p. 54—55° (*amide*, m.p. 143—144°); the *Et* ester, b.p. 95—97°/0·8 mm., could not be condensed with $Et_2C_2O_4$ in presence of KOEt, CPh_3Na, or Mg mesityl bromide. H. W.

Lactones related to the cardiac aglycones. VI. Action of diazomethane on derivatives of 2-pyrone. J. Fried and R. C. Elderfield (*J. Org. Chem.*, 1941, **6**, 577—583).—2-Pyrone-5-carboxylic acid is transformed by pure, boiling $SOCl_2$ into the *chloride* (I), m.p. 77°, the structure of which is established by its conversion into the corresponding Me ester (II). (I) is transformed by CH_2N_2 at −10° then at 0—2°, and finally at room temp. into 5-ω-*diazoacetyl*-, m.p. 76—77°, converted by glacial AcOH at 95° into 5-*acetoxyacetyl*-, m.p. 97—98°, and by HCl in anhyd. dioxan–Et_2O into 5-ω-*chloroacetyl*-, m.p. 65—66°, -6-*methyl*-2-*pyrone*. Similarly (II) and CH_2N_2 in MeOH–Et_2O at 0° and then at room temp. yield *Me* 6-*methyl*-2-*pyrone*-5-*carboxylate* (III), m.p. 86—87°, with a red oil which could not be crystallised and was not further examined. Hydrogenation (PtO_2 in MeOH) of (III) leads to a neutral material of pleasant odour, and (mainly) α-*ethylglutaric acid*, m.p. 58—59° (*dianilide*, m.p. 188—190°), identical with a sample prepared by hydrolysis and decarboxylation of the product obtained from $CHMeBr{\cdot}CO_2Et$ and $CHEt(CO_2Et)_2$. Analogously, (II) is hydrogenated and the product is hydrolysed (boiling conc. HCl) to α-methylglutaric acid, m.p. 77° (*dianilide*, m.p. 179—180°). An electronegative substituent at $C_{(5)}$ in the pyrone nucleus appears necessary for the entry of Me at $C_{(6)}$ under the influence of CH_2N_2. Thus 5-methyl-2-pyrone fails to react with CH_2N_2 and the unchanged material is hydrogenated to an *iso*hexoic acid analysed as the *piperazonium* salt, m.p. 115—116°. H. W.

Coumarone derivatives.—See B., 1941, II, 408.

Constitution of usnic acid. II. C. Schöpf and F. Ross (*Annalen*, 1940, **546**, 1—40; cf. A., 1928, 294).—Structures proposed by Robertson are confirmed and those for related substances expounded. Decarbousnic acid diacetate and O_3 in CCl_4 give an *ozonide* (I), m.p. 148°, converted by boiling 3% MeOH–HCl or other reagents into 3 : 5-*diacetylphloroglucinol* 2 : 6-*diacetate* (II), m.p. 116°, sublimes at 110°/12 mm., and $CH_2Ac{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$ (isolated as the CH_2 compound from triacetolactone; p-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ gives a compound, m.p. 100°,



(I.)

clear at 135°). With Ac_2O–NaOAc, (II) gives the *triacetate*, m.p. 95°, with $NHPh{\cdot}NH_2$ gives the *compound*, $C_{19}H_{20}O_5N_2$, m.p. 196°, and is also obtained from 2 : 6 : 1 : 3 : 5 : 4-$(OH)_2C_6MeAc_2{\cdot}OAc$ by Ac_2O–C_5H_5N. *d*- or *dl*-Usnic acid piacetate and O_3 in CCl_4 give an *ozonide*, m.p. 152—153° (decomp.; gas) [and an amorphous substance (III)], which in boiling 96% EtOH gives CO_2, 6-*acetyl*-3 : 5-*diacetoxy*-2 : 4-*dimethylcoumaran*-1-*one* (IV), m.p. 132°, α 0°, and $CH_2Ac{\cdot}CO{\cdot}CO_2Et$ (V) [isolated by condensation with *o*-$C_6H_4(NH_2)_2$ to the *compound*, *o*-$C_6H_4{<}^{NH{\cdot}CO}_{N{=}C{\cdot}CH_2Ac}$, m.p. 257°, also obtained from pure (V)]. In conc. H_2SO_4 at room temp. or boiling 3% HCl–MeOH, (IV) gives, by hydrolysis and rearrangement, 3 : 5-*dihydroxy*-4-*acetyl*-2 : 7-*dimethylcoumaran*-1-*one* (VI), m.p. 223° after sintering and becoming violet at 195° (*diacetate*, m.p. 131—132°). In EtOH, (III) gives a *polymeride* (? isomeride), m.p. 222—223°, of (IV), also converted into (VI) by H_2SO_4. *d*-Usnic acid, obtained from the diacetate by NaOH, has m.p. 202—204° (cf. *loc. cit.*). R. S. C.

Methylation of quercetagetin. P. S. Rao (*Proc. Indian Acad. Sci.*, 1941, **14**, A, 35—36).—Quercetagetin (I) is converted into its Me_6 ether (II), m.p. 142—144°, in ~90% yield by treating the solution of the acetate in $COMe_2$ with small alternate quantities of Me_2SO_4 and 20% NaOH; the solution is finally made definitely alkaline, left overnight, and then acidified. (II) is also obtained in 80% yield by gradually adding ethereal CH_2N_2 to (I) in anhyd. MeOH or dioxan. Addition of anhyd. K_2CO_3 to (I) in dry $COMe_2$ causes almost complete pptn. of the pigment and subsequent boiling of the mixture with MeI does not cause any methylation; with a mixture of $COMe_2$ and dioxan much (I) is pptd. but MeI causes the formation of 3 : 6 : 7 : 3′ : 4′-pentamethylquercetagetin in poor yield. H. W.

Additive compounds of 1 : 4-dioxan with zinc, cadmium, cobalt, and nickel halides. H. Rheinboldt. **Compounds of 1 : 4-dioxan with metal halides.** L. F. Yntema (*J. Amer. Chem. Soc.*, 1941, **63**, 2535).—Concerning priority (A., 1941, II, 74; 1937, II, 174, 318). R. S. C.

Picolinic acid derivatives.—See B., 1941, II, 408.

Constitution of 2-sulphanilamidopyridine. M. A. Phillips (*Nature*, 1941, **148**, 409, 466).—The constitution of 2-sulphanilamidopyridine (I) is discussed (cf. A., 1940, II, 188). Further evidence bearing on structure is the formation of *p*-aminobenzenesulphonyl-2-pyridylglycineamide (II) when (I) is treated with alkaline $CH_2Cl{\cdot}CO{\cdot}NH_2$. Hydrolysis (NaOH) of (II) gives *p*-aminobenzenesulphonyl-2-pyridylglycine which with hot, dil. mineral acid yields 2-*pyridylglycine*. L. S. T.

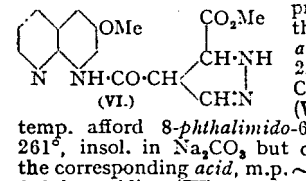
Chemistry of vitamin-B_6 III. 3-Hydroxy-4 : 5-di(hydroxymethyl)-2-ethylpyridine, a homologue of vitamin-B_6. S. A. Harris and A. N. Wilson (*J. Amer. Chem. Soc.*, 1941, **63**, 2526—2527; cf. A., 1941, II, 268).—Methods previously described (A., 1939, II, 340) lead successively to α-*methoxyhexane*-βδ-*dione* (from COMeEt, $OMe{\cdot}CH_2{\cdot}CO_2Me$, and Na), b.p. 69·5—70°/7·5 mm. (by $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$–piperidine–EtOH), 2-*hydroxy*-3-*cyano*-4-*methoxymethyl*-6-*ethylpyridine* (I), m.p. 190—191° (converted by 50% H_2SO_4 into 2-*hydroxy*-4-*hydroxymethyl*-6-*ethylpyridine*-3-*carboxylic lactone*, m.p. 285°), (by HNO_3–Ac_2O) the 5-NO_2-derivative, m.p. 171—172°, of (I), (by PCl_5) 2-*chloro*-5-*nitro*-3-*cyano*-4-*methoxymethyl*-6-*ethylpyridine*, m.p. 56—57°, (by H_2–Pd–HCl) 3-*amino*-5-*aminomethyl*-4-*methoxymethyl*-2-*ethylpyridine dihydrochloride*, m.p 214°, 3-*hydroxy*-5-*hydroxymethyl*-4-*methoxymethyl*-2-*ethylpyridine hydrobromide*, m.p. 196°, and (by H_2O–AgCl) 3-*hydroxy*-4 : 5-*di*(*hydroxymethyl*)-2-*ethylpyridine hydrochloride* (II), m.p. 192°. 100 μg. of vitamin-B_6 is curative in all cases within 14 days, 50 μg. in 75% of the cases, and 25 μg. causes partial healing. It is 200 times as active as (II). R. S. C.

Synthetic experiments with 3- and 4-aminoquinaldines. F. Lions and E. Ritchie (*J. Proc. Roy. Soc. New South Wales*, 1940, **74**, 443—449).—4-Aminoquinaldine does not condense with $CH_2Ac{\cdot}CO_2Et$ (HCl), CH_2Ac_2, or $(CH_2Ac)_2$, but with $CH_2Ac{\cdot}CO_2Et$ at 160° yields 4-*acetoacetamidoquinaldine*, m.p. 256° (decomp.), cyclised (conc. H_2SO_4) to 2-*hydroxy*-4 : 5-*dimethyl*-, decomp. ~290° (darkens ~280°), with As_2O_5, glycerol, and H_2SO_4 at 140—150°, 5-methyl-, m.p. 206° [picrate, m.p. 245—246° (decomp.)], and with conc. HCl, $ZnCl_2$, and par-

acetaldehyde, 2 : 5-dimethyl-, m.p. 95—96°, -7 : 8-benzo-1 : 6-naphthyridine [picrate, m.p. 225° (decomp.)] (cf. Marckwald, A., 1894, i, 474). 3-Aminoquinaldine gives no crotonic ester with $CH_2Ac{\cdot}CO_2Et$, but with *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ yields *3-salicylideneaminoquinaldine*, m.p. 139°, with $CH_2Ac{\cdot}CO_2Et$ at 160°, *3-acetoacetamidoquinaldine*, m.p. 149° (which could not be cyclised), with $(CH_2Ac)_2$ in boiling AcOH–EtOH, *N-3′-quinaldyl-2 : 5-dimethylpyrrole*, m.p. 71° (*picrate*, m.p. 190°), with $CH_2Bz{\cdot}CHAc{\cdot}CO_2Et$ in boiling AcOH–EtOH, *Et N-3′-quinaldyl-2-phenyl-5-methylpyrrole-4-carboxylate*, m.p. 166°, and with CH_2Ac_2 in boiling AcOH–EtOH, *β-3-quinaldylpropenyl Me ketone*, m.p. 96°, which could not be cyclised. 2-Methylquinoline-3 : 4-dicarboxylic imide with Na in EtOH, then $CH_2Br{\cdot}CO_2Et$, yields *Et 2-methylquinoline-3 : 4-dicarboxylimidoacetate*, m.p. 159°, which with NaOMe in MeOH at 100° yields *Me 5-methyl-1 : 4-diketo-7 : 8-benzo-1 : 2 : 3 : 4-tetrahydro-3 : 6-naphthyridine-2-carboxylate* (?), m.p. >300° (sinters and chars at 235°). A. Li.

New synthesis of *iso*quinoline derivatives. K. N. Gaind, S. Kapoor, and J. N. Ray (*J. Indian Chem. Soc.*, 1941, **18**, 213—216; cf. A., 1932, 1262).—The oxime of piperonylacetone (prep. by reducing piperonylideneacetone; *semicarbazone*, m.p. 166°) undergoes Beckmann transformation ($POCl_3$ in PhMe) giving 1-methylnorhydrastinine (**I**). In EtOH containing piperidine, (**I**) condenses with piperonal, veratraldehyde, anisaldehyde, and cotarnine [1 mol. of (**I**) : 1 mol. of aldehyde], and EtCHO, $COMe_2$ ($ZnCl_2$), and MeCHO [2 mols. of (**I**) : 1 mol. of aldehyde or ketone], giving products having *picrates*, m.p. 156°, 126° (decomp.), 192° (decomp.), 237°, 223°, 180°, and 172° (decomp.), respectively. A. Li.

Condensation of heterocyclic amines with dicarboxylic acid anhydrides. D. Shapiro and F. Bergmann (*J. Org. Chem.*, 1941, **6**, 774—779).—8-Amino-6-methoxyquinoline (**I**) does not react with $(CH_2{\cdot}CO_2H)_2$ in boiling dioxan but is transformed by $(\cdot CH_2{\cdot}CO)_2O$ (**II**) in boiling C_6H_6 into *8-β-carboxypropionamido-6-methoxyquinoline* (**III**), m.p. 151° (decomp.) (*Me* ester, m.p. 127—128°). At 120° (**I**) and (**II**) yield *succin-6-methoxy-8-quinolinylimide* [*N-6-methoxy-8-quinolylsuccinimide*] (**IV**), m.p. 178°, and *succindi-6-methoxy-8-quinolylamide*, m.p. 258°. At 180° the same result is obtained. At 120° with 5 equivs. of (**II**) only (**III**) appears to be formed. It is readily hydrolysed by 5% NaOH at 100° to (**III**). At 120° or in boiling xylene (**I**) and $(CH{\cdot}CO)_2O$ (**V**) give only tarry products whereas in boiling C_6H_6 they produce *8-β-carboxyacrylamido-6-methoxyquinoline*, m.p. 225° (decomp.), converted by CH_2N_2 into (**VI**). *o*-$C_6H_4(CO)_2O$ (**VII**) and (**I**) in dioxan at room temp. afford *8-phthalimido-6-methoxyquinoline* (**VIII**), m.p. 261°, insol. in Na_2CO_3 but converted by 10% NaOH into the corresponding *acid*, m.p. ~70° with re-formation of (**VIII**). Sulphapyridine (**IX**) and (**II**) in dioxan at 100° yield *2-p-β-carboxypropionamidobenzenesulphonamidopyridine* (**X**), m.p. 145°, whereas at 140° without solvent the product is the *imide*, m.p. 288—290°, immediately converted by cold NaOH or warm Na_2CO_3 into (**X**). (**IX**) and (**V**) in dioxan at 100° or without solvent, at 120° or 190° afford *2-p-β-carboxyacrylamidobenzenesulphonamidopyridine*, m.p. 208°, which is stable at 205°. (**IX**) and (**VII**) in boiling dioxan give *2-p-o′-carboxybenzamidobenzenesulphonamidopyridine*, m.p. 276°, whereas at 190° the reactants yield the corresponding imide, m.p. 276°, easily hydrolysed by cold NaOH. The solubilities of these substances in conc. and dil. HCl and AcOH are tabulated.


(VI.)

H. W.

Nitrogen compounds in petroleum distillates. XXIII. Isolation of 2 : 3- and 2 : 4-dimethylbenzo[*h*]quinoline from California petroleum. L. M. Schenck and J. R. Bailey (*J. Amer. Chem. Soc.*, 1941, **63**, 2331—2333; cf. A., 1941, II, 269).—The bases, b.p. 365°, from California petroleum yield, by cumulative extraction with 1 : 1·2 (vol.) 6N-HCl–$CHCl_3$ and then multiple acid extraction, 2 : 3-*dimethyl-α-naphthoquinoline* (**I**), m.p. 83—84° (nitrate; picrate, m.p. 228—229°; *H sulphate*, m.p. 265—267°), oxidised by SeO_2 in boiling EtOH to an aldehyde, whence H_2O_2 yields *3-methyl-α-naphthoquinoline-2-carboxylic acid*, m.p. 162—163°. The bases, b.p. 355°, yield by cumulative and then countercurrent acid extraction, 2 : 4-*dimethyl-α-naphthoquinoline* (**II**), m.p. 55—56° [*H sulphate*, m.p. 227—228°; *picrate*, m.p. 230—231°; *nitrate*, m.p. 173° (decomp.)], oxidised (as above) to α-naphthoquinoline-2 : 4-dicarboxylic acid (trace) (*Ag*$_2$ salt). With tiglaldehyde and conc. HCl at 100°, α-$C_{10}H_7{\cdot}NH_2$ gives (**I**) and with CH_2Ac_2 gives (**II**). M.p. are corr. R. S. C.

Syntheses with 2-bromo-5-nitroacetophenone.—See A., 1942, II, 16.

1-Hydroxyacridine as a chelate compound. D. H. Freeman and F. Lions (*J. Proc. Roy. Soc. New South Wales*, 1940, **74**, 520—526).—Dil. aq. solutions of metallic salts containing NaOAc and AcOH with 1-hydroxyacridine yield H_2O-insol. *Cu*^{II}, *Pb*, *Fe*^{II} [from $Fe(NH_4)_2(SO_4)_2$ or $FeCl_3$], *Ni*^{II} (+H_2O), *Zn* (+2H_2O), *Co*^{II}, *Mn*^{II}, and *Cd bis-1-acridylate*. $Cr_2(SO_4)_3$ similarly yields a *complex*, $[Cr(C_{13}H_8ON)_2(H_2O)_2]OAc$. Ppts. from Hg^I, Hg^{II}, and Tl^{III} salts are insol., those from Ca and UO_2^{II} salts (in neutral) and from Ba, Ca, and Mg salts (in alkaline solution) sol., in dil. AcOH–NaOAc. Pb and Cu in concns. of 10^{-4} and 10^{-6} g. per c.c. respectively give definite ppts. Al, Sn^{II}, and Bi salts give no ppts. A. Li.

Cleavage of glyoxaline ring of histidine and carnosine by bromine. E. T. Mertz (*Proc. Soc. Exp. Biol. Med.*, 1941, **47**, 312—315).—If histidine is treated with Br at p_H 1—1·5 all the ring-N and almost half the α-NH_2-N is recovered as NH_3. Cu carnosine, Cu acetylhistidine, and glyoxalinyl-lactic acid, similarly treated, give off all the ring-N as NH_3. Other compounds examined gave smaller quantities. V. J. W.

Ultra-violet absorption spectra of barbituric acid derivatives. II. Barbitone and phenobarbitone and their methyl derivatives. R. E. Stuckey (*Quart. J. Pharm.*, 1941, **14**, 217—225; cf. A., 1941, II, 148).—The absorption spectra of barbitone (**I**), phenobarbitone (**II**), and their 1-Me and 1 : 3-Me_2 derivatives in acid, alkaline, and aq. solution have been determined. In aq. alkaline solution (**I**) and (**II**) are present as salts. The Na_1 derivative of (**I**) is almost completely enolised in M./4000 solution. Methylation of (**I**) with NaOH–Me_2SO_4 produces only *N*-Me compounds. H. G. R.

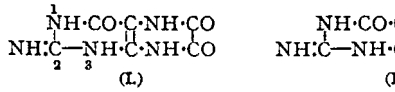
Pinacolonylbarbituric acids. S. M. McElvain and R. F. Taylor (*J. Amer. Chem. Soc.*, 1941, **63**, 2513—2516).—$COMeBu^{\gamma}$ and $CO(CO_2Et)_2$ at, best, 160° give *Et*$_2$ *pinacolonyltartronate* [*α-hydroxy-γ-keto-δδ-dimethylpentane-αα-dicarboxylate*] (**I**) (83%; catalysts are not effective), b.p. 111—112°/1 mm., stable to P_2O_5 at 68° or I at 225°, dehydrated by anhyd. HBr–C_6H_6 or PBr_3–xylene (74—78%) or basic reagents (best, $KOBu^{\gamma}$–$Bu^{\gamma}OH$ at room temp.; 52%) to *Et*$_2$ *γ-keto-δδ-dimethyl-Δ*$^{\alpha}$*-pentene-αα-dicarboxylate* (**II**), b.p. 105—106°/1 mm. $NaCPh_3$ converts (**I**) in Et_2O into $CHPh_3$, a tar, and only a little (**II**). Br–CCl_4 and aq. $KMnO_4$ react readily with (**II**). Alkali polymerises (**II**) with development of a red colour. After removal of traces of Br by boiling (0·01 mm.) with Raney Ni, (**II**) is readily (room temp./100 atm.; later 100°) hydrogenated (Raney Ni) to give *Et*$_2$ *γ-keto-δδ-dimethylpentane-αα-dicarboxylate* (**III**) (88%), b.p. 106—107°/1 mm., and *Et δ-keto-εε-dimethyl-n-hexoate* (9%), b.p. 104—105°/11 mm. With RBr–NaOEt–EtOH, (**III**) gives *Et*$_2$ *γ-keto-δδ-dimethyl-α-ethyl-* (78%), b.p. 106—107°/1 mm., *-α-allyl-* (90%), b.p. 107—108°/1 mm., and *-α-isoamyl-pentane-αα-dicarboxylate* (78%), b.p. 114—115°/1 mm. Thence NaOEt–EtOH and $CO(NH_2)_2$ yield *5-ethyl-* (42%), m.p. 204—205°, and *5-allyl-5-pinacolonylbarbituric acid* (40%), m.p. 190—191°. Similarly, NaOPr$^{\beta}$–Pr$^{\beta}$OH and $CO(NH_2)_2$ give a 73% yield of *5-isoamyl-5-pinacolonylbarbituric acid*, m.p. 209—210°. These acids have lower therapeutic indices than has amytal. R. S. C.

Structure of proteins. Synthesis of compounds of amino-acids with diketopiperazine. C. N. Lerman and N. I. Gavrilov (*J. Gen. Chem. Russ.*, 1941, **11**, 127—132).—Diketopiperazine (**I**) and $CH_2Br{\cdot}COCl$ in xylene (at the b.p.) yield *di-(N-bromoacetyl)diketopiperazine*, m.p. 148—149° This does not react with urethane or $NH_2{\cdot}CO_2CH_2Ph$, whilst with liquid NH_3 it yields (**I**) and $NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2$; di-(*N*-chloroacetyl)diketopiperazine reacts similarly with NH_3, whilst with NaOAc in EtOH (20 hr. at the b.p.) the products are (**I**) and $CH_2Ac{\cdot}CO_2Et$. Attempts to cyclise various tripeptides did not lead to production of compounds of NH_2-acids with (**I**). R. T.

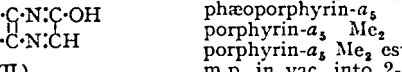
Pyrimidines. CLXXIV. Action of dibromohydroxyhydrouracil on malonic and barbituric acids. T. B. Johnson and (Miss) M. G. Winton (*J. Amer. Chem. Soc.*, 1941, **63**, 2379—2381).—5 : 5-Dibromo-4-hydroxyhydrouracil with (*a*) $CH_2(CO_2H)_2$ or (*b*) barbituric acid in H_2O gives 5-bromouracil and (*a*) $CBr_3{\cdot}CO_2H$ or (*b*) hydurilic acid. R. S. C.

Sulphapyrazine, sulphapyrimidine, and "sulphadiazine." R. C. Ellingson (*J. Amer. Chem. Soc.*, 1941, **63**, 2524—2525).—2-Aminopyrazine and *p*-NHAc·C_6H_4·SO_2Cl in C_5H_5N give 2-N^4-*acetylsulphanilamide*, m.p. 250—252° (decomp.), hydrolysed by acid to 2-*sulphanilamidopyrazine*, m.p. 255—257° (decomp.) (*Na* salt, + H_2O, has p_H 9·3 in 10% aq. solution). Possible confusion in nomenclature is noted. R. S. C.

Wing-pigments of butterflies. X. Synthesis of xanthopterin. R. Purrmann (*Annalen*, 1940, **546**, 98—102).—4 : 5-Diamino-2 : 6-dihydroxypyrimidine and $H_2C_2O_4$ at 260° give *deiminoleucopterin* (I) (62%). The 3-*Me* derivative is similarly



(I.)



(II.)

obtained at 240°. 2 : 4 : 5-Triamino-6-hydroxypyrimidine and $CHCl_2$·CO_2H at 120° give the 5-*CHCl*$_2$·*CO*·*NH*-compound, decomp. ~225°, which with, first, AgOAc and then Ag_2CO_3 in boiling H_2O gives 10% of xanthopterin, thus shown to be (II). Dehydrogenation of the synthetic Ba salt of (II) by Pt in aq. AcOH yields leucopterin. (All quantities micro.) R. S. C.

Chlorophyll. XCIX. Optically active hæmotricarboximide from chlorophyll. H. Fischer and H. Wenderoth (*Annalen*, 1940, **545**, 140—147; cf. A., 1939, II, 128).—A solution of phæophorbide *a* or the corresponding *meso*-compound in 50 vol.-% H_2SO_4 is gradually treated with aq. CrO_3 at −12°, kept at 0° and then at room temp., and the product is separated into basic and acidic fractions (*loc. cit.*) The latter material yields only non-cryst. matter when sublimed in a high vac. and is further purified by treatment with $PbCO_3$ and NH_3, whereby brown impurities, $H_2C_2O_4$, and hæmatic anhydride are removed as a sparingly sol. fraction. The more freely sol. Pb salts are transformed into the Ag compounds, whereby ultimately a fraction with $[\alpha]^{20}_{680-730}$ −15° in H_2O (calc. on Ag salt; −30° calc. on free hæmotricarboximide) is obtained. The imide derived therefrom did not crystallise. The *Ag* salt of *r*-hæmotricarboximide is described incidentally. H. W.

Chlorophyll. C. Transformation of dehydrobacteriophæophorbide-*a* into chlorophyll-*a*. H. Fischer, H. Mittenzwei, and D. B. Hevér (*Annalen*, 1940, **545**, 154—178).—Al(OPr$^\beta$)$_3$ is obtained by heating pure Al foil with Pr$^\beta$OH (technical product, boiled under reflux for 4 hr. with CaO and distilled) containing a little $HgCl_2$ until dissolution is complete. The mixture is kept overnight at 70° and then decanted from a ppt.; in absence of moisture the clear solution can be kept for long periods. Technical Al gives undesired Cu and Zn salts which diminish the yields and render purification difficult. In many cases, however, reduction of CO in the isocyclic ring succeeds only in presence of Cu or Zn salts. The substance, dissolved in Pr$^\beta$OH or C_6H_6 if necessary, is boiled with the reagent in a special apparatus until $COMe_2$ cannot be detected by 2 : 4 : 1-$(NO_4)_2C_6H_3$·NH·NH_2 in the distillate. The use of a current of inert gas is helpful and sometimes necessary but it complicates the detection of $COMe_2$. All compounds of the chlorophyll series containing Ac (reduced to ·CHMe·OH) at $C_{(2)}$ and hence all ketoporphyrins and, especially, bacterio- and $\Delta^{3:4}$-dehydrobacterio-derivatives are particularly suited to treatment with Al(OPr$^\beta$)$_3$. CHO at $C_{(3)}$ of the *b*-derivatives is readily reduced to CH_2·OH. The behaviour of CO at $C_{(9)}$ of the isocyclic ring is not uniform. Phæophorbides of the *a*- and *b*-series generally react with great difficulty and the formation of the corresponding 9-OH-substances can usually be detected only if Zn or Cu salts are present in the reagent. The yields are exceedingly small. The 9-CO group of pyrocompounds and hence in phæophorbides decarboxylated at $C_{(10)}$ is easily reduced with resulting good yields. Analogously with the relationships in the prep. of oximes, Ac or CHO simultaneously present at $C_{(2)}$ or $C_{(3)}$ respectively is first reduced and CO is affected only when the change is protracted. Separation of the mixtures is best effected chromatographically since the vals. obtained by HCl extraction of nearly all the prepared carbinols are not confined within narrow limits. The compounds do not crystallise well. No difference could be detected between the behaviour of free and esterified derivatives. The following reductions are described: methylphæophorbide-*a* (I) to 9-hydroxydeoxomethylphæophorbide-*a* (II) in very small yield, reduced to zero when pure Al(OPr$^\beta$)$_3$ is used; the Zn complex salt of (I) to (II) in 5% yield; methylpyrophæophorbide-*a* to 9-*hydroxydeoxomethylpyrophæophorbide*-a, m.p. 245°, in ~50% yield; methylphæophorbide-*b* to a mixture of *methylphæophorbide*-b-3-*methanol*, m.p. >300°, and 9-hydroxydeoxomethylphæophorbide-*b*-3-methanol (in so small proportion that a pure spectroscopic sample could not be isolated); rhodin g_7 Me_3 ester to the -3-*methanol*, m.p. 184—186°, in 50% yield; mesopyrophæophorbide-*b* Me ester first to mesopyrophæophorbide-*b* Me ester 3-methanol, m.p. 226°, and then to 9-*hydroxydeoxomesopyrophæophorbide*-b *Me ester* 3-*methanol*: purpurin-7 Me_3 ether to (?) vinylrhodoporphyrin, m.p. 220° (lit. m.p. 276°); phæoporphyrin-a_5 Me_2 ester to 9-hydroxydeoxophæoporphyrin-a_5 Me_3 ester, m.p. ~288°; ketophæoporphyrin-a_5 Me_2 ester to (mainly) 2-α-hydroxyphæoporphyrin-a_5 Me_2 ester, m.p. ~270° (which passes above its m.p. in vac. into 2-vinylphæoporphyrin-a_5), and 2 : α : 9-dihydroxydeoxophæoporphyrin-a_5 Me_2 ester; ketochloroporphyrin-e_6 Me_3 ester, obtained by the action of Fe powder and 90% HCO_2H followed by $FeCl_3$ in MeOH on 2-acetylchlorin-e_6 Me_3 ester, to 2-α-hydroxychloroporphyrin-e_6 Me ester, m.p. 247°, in good yield (passing above its m.p. in a high vac. into 2-vinylphæoporphyrin-a_5 Me_2 ester); "synthetic" 2-acetyl-2-devinylmethylphæophorbide-*a* to (mainly) 2-α-hydroxymesomethylphæophorbide-*a* (III), m.p. 224—225°; natural 2-acetyl-2-devinylmethylphæophorbide *a* [dehydrobacteriomethylphæophorbide-*a*] to (III) and 2-α-hydroxymeso-9-hydroxydeoxomethylphæophorbide-*a*; "natural" 2-acetyl-2-devinylchlorin-e_6 Me_3 ester [dehydrobacteriochlorin-e_6 Me_3 ester] to 2-α-hydroxymesochlorin-e_6 Me_3 ester, m.p. 204°, which passes at 220—230° into chlorin-e_6 Me_3 ester (IV). Little or no reaction is observed with mesomethylphæophorbide-*a* or (IV). H. W.

Chlorophyll. CI. Rotatory dispersion and apparent inactivity of chlorophyll derivatives. F. Pruckner, A. Oestreicher, and H. Fischer. **CII. Partial syntheses of methylphæophorbid-*a* from chlorin-e_6 triester.** H. Fischer and A. Oestreicher (*Annalen*, 1940, **546**, 41—49, 49—57).—CI. The apparent optical inactivity of chlorophyll derivatives is due to the great rotatory dispersion, often involving changes of sign for α. When white light is used, the λλ transmitted depend on the concn. of the solution and length of the column of liquid and α varies accordingly. Approx. measurements and colours are given for 13 derivatives at various concns. Synthetic and natural products behave identically.

CII. When chlorin-e_6 Me_3 ester (I) in C_5H_5N is added to boiling 30% KOH–MeOH and the reaction is stopped after 2—3 sec. by addition to aq. HCl–ice, 40% of methylphæophorbide-*a* (II), m.p. 228°, is obtained. Boiling (I) for 0·5 hr. in NaOMe–MeOH–$COMe_2$ and subsequent treatment with CH_2N_2 also gives (II). Further treatment of (II) by either method gives chlorin-e_6 (III), thus confirming the mechanism of formation of (III) directly from (I). KOPr–PrOH and (II) give purpurin-7 Me_3 ester. Similar reactions are reported for other compounds, in detail for conversion of chloroporphyrin-e_6 Me_3 ester into phæoporphyrin-a_5 Me_2 ester (85%) and thence into chloroporphyrin-e_6. R. S. C.

Spectra of porphyrins and their acid salts. S. Aronoff and C. A. Weast (*J. Org. Chem.*, 1941, **6**, 550—557).—Spectroscopic investigation of ætioporphyrin III, mesoporphyrin IX, phylloerythrin (I), and deoxophylloerythrin reveals no change in acid form with increasing acidity up to 96% H_2SO_4 except where additional structures may be formed and the resonances increased, as oxonium formation on the ketonic O of (I). "Intermediate" types of porphyrin spectra are shown to be mathematically deducible by the addition of the acid and free base curves, assuming a salt : free base ratio. The existence of porphyrin mono-salts must be limited within a narrow range of acidity. H. W.

Bile pigment production *in vitro*. M. Engel (*Z. physiol. Chem.*, 1940, **266**, 135—148).—By coupled oxidation of ox hæmoglobin (I) with O_2 in presence of ascorbic acid, verdohæmoglobin (II) is formed. The latter is quantitatively split by AcOH–Et_2O into biliverdin (III), which is reduced by Zn in aq. NH_3 to bilirubin, which may be determined spectroscopically. Catalase inhibits the formation of (II). Periodic arterialisation and "reduction" of (I) does not yield more (II) than simple shaking with O_2. The hypothesis that gas exchange under physiological conditions is responsible for the degradation of (I) to bile pigment is untenable. Only 10% of the hæm of (I) could be converted into (III). Other

pyrroles are formed from (I) when oxidised with O_2 and ascorbic acid. J. H. B.

[Reinvestigation of the configuration of hæmin.] H. Fischer and F. Endermann (*Annalen*, 1940, **545**, 148—153). —A reply to criticisms. Condensation of 5-formyl-2 : 3-dimethylpyrrole with 2 : 4-dimethylpyrrole (I) in EtOH–48% HBr gives 4 : 5 : 3′ : 5′-tetramethylpyrromethene hydrobromide *A* (II), decomp. 217—218°, identical with a product obtained from 5-formyl-2 : 4-dimethylpyrrole and 2 : 3-dimethylpyrrole. The free *base* (III) has m.p. 83—84°. 5-Formyl-2 : 4-dimethylpyrrole and (I) in EtOH–48% HBr afford 3 : 5 : 3′ : 5′-*tetramethylpyrromethene hydrobromide* C (IV), decomp. 248° [free *base* (V), m.p. 118°]. 4 : 5 : 4′ : 5′-Tetramethylpyrromethene hydrobromide (VI), decomp. 207—208°, yields the *base* (VII), m.p. 124—125°. Depressions of m.p. are observed with mixture of (II), (IV), and (VI) and with those of (III), (V), and (VII). (II) is therefore stated to be a homogeneous material and not a mixture of (II), (IV), and (VI) as suggested by Corwin as a possibility. H. W.

5 : 5-Dialkyloxazolidine-2 : 4-diones. R. W. Stoughton (*J. Amer. Chem. Soc.*, 1941, **63**, 2376—2379).—Addition of aliphatic CORR′ (1 mol.) and a little piperidine to HCN (1·2 mol.) at 0° and hydrolysis of the crude product by 90% H_2SO_4 at 0° gives OH·CRR′·CO·NH_2, hydrolysed by 20% NaOH or HCl to the acid; the derived (HCl) Et ester with $CO(NH_2)_2$ and NaOEt–EtOH gives 2 : 4-diketo-5 : 5-dialkyloxazolidines (*A*). Mixed aryl–alkyl compounds are similarly prepared except that the cyanohydrins are hydrolysed by HCl–Et_2O at 0°. Thus are prepared : *α-hydroxy-α-methyl*-n-*hexoic*, m.p. 32—33° (Et ester, b.p. 100—101°/24 mm.; *amide*, m.p. 57—58°), -n-*heptoic*, m.p. 44—45° (Et ester, b.p. 112—113°/23 mm.; *amide*, m.p. 64—65°), -*n*-octoic, m.p. 39—40° (Et ester, b.p. 101—102°/5 mm.; *amide*, m.p. 58—59°), -*n*-nonoic, m.p. 40—41° (Et ester, b.p. 103—104°/5 mm.; *amide*, m.p. 78—79°), -*n*-decoic, m.p. 42—43° (Et ester, b.p. 121—122°/5 mm.; *amide*, m.p. 78—79°, and -*n*-undecoic acid, m.p. 46—47° (Et ester, b.p. 125—127°/3 mm.; *amide*, m.p. 86—87°); α-hydroxy-*αγγ*-trimethyl-*n*-valeric, m.p. 108—109° (Et ester, b.p. 92—93°/20 mm.; *amide*, m.p. 115—116°), *α-hydroxy-αδ-dimethyl*-n-*octoic*, m.p. 47—48° (Et ester, b.p. 112—114°/9 mm.; *amide*, m.p. 38—39°), α-hydroxy-α-*n*-propyl-*n*-valeric, m.p. 81—82° (Et ester, b.p. 113—115°/30 mm.; *amide*, m.p. 69—70°), α-hydroxy-α-*n*-butyl-*n*-hexoic, m.p. 87—88° (Et ester, b.p. 114—116°/10 mm.), α-hydroxy-δ-methyl-α-*iso*-butyl-*n*-valeric, m.p. 128—129° (Et ester, b.p. 105—106°/5 mm.; *amide*, m.p. 138—139°), *α-hydroxy*-α-n-*amyl*-n-*heptoic*, m.p. 76—77° (Et ester, b.p. 128—129°/5 mm.; *amide*, m.p. 92—93°), *α-hydroxy-α-phenyl*-n-*valeric*, m.p. 93—94° (Et ester, b.p. 124—125°/3 mm.; *amide*, m.p. 131—132°), -n-*hexoic*, m.p. 102—103° (Et ester, b.p. 130—132°/4 mm.; *amide*, m.p. 81—82°), and -n-*heptoic*, m.p. 102—103° (Et ester, b.p. 143—145°/4 mm.; *amide*, m.p. 93—94°), and *α-hydroxy-α-phenyl-δ-methyl*-n-*valeric acid*, m.p. 112—113° (Et ester, b.p. 126—128°/4 mm.; *amide*, m.p. 129—130°); 2 : 4-*diketo-5-methyl*-5-n-*butyl*-, b.p. 148—151°/4 mm., -n-*amyl*-, m.p. 25°, b.p. 149—150°/3 mm.; -*neopentyl*- [*ββ-dimethyl*-n-*propyl*-], m.p. 55—56°, -n-*hexyl*-, m.p. 46—47°, b.p. 149—150°/2 mm., -n-*heptyl*-, m.p. 32—33°, b.p. 155—156°/2 mm., -*γ-methyl*-n-*hexyl*-, b.p. 168—169°/3 mm., -n-*octyl*-, m.p. 62—63°, and -n-*nonyl*-, m.p. 52—53°, -*oxazolidine*; 2 : 4-diketo-5 : 5-dimethyl-, m.p. 70—77°, -ethyl-, m.p. 28°, b.p. 146—147°/6 mm., -n-*propyl*-, m.p. 42—43°, b.p. 141—143°/3 mm., -n-*butyl*-, m.p. 68—69°, -iso*butyl*-, b.p. 150—151°/3 mm., -n-*amyl*-, m.p. 63—64°, and -*phenyl*-, m.p. 135—136°, -*oxazolidine*; 2 : 4-diketo-5-phenyl-5-methyl-, m.p. 73—74° (lit. 70°), b.p. 169—171°/3 mm., -ethyl-, m.p. 61—62° (lit. 63°), b.p. 174—176°/3 mm., -n-*propyl*-, b.p. 176—178°/2 mm., -n-*butyl*-, m.p. 63—64°, b.p. 181—182°/2 mm., -iso*butyl*-, b.p. 184—186°/3 mm., and -n-*amyl*-, b.p. 199—200°/3 mm., -*oxazolidine*. *α-Hydroxy-αββ-trimethyl*-n-*butyramide*, m.p. 145—146°, and *α-hydroxy*-α-iso*propyl*iso*valeramide*, m.p. 116—117°, resist hydrolysis; with $ClCO_2Et$ in boiling PhMe they give 2 : 4-*diketo-5-methyl*-5-tert.-*butyl*- (65%), m.p. 85—86°, and -5 : 5-*diiso*propyl-*oxazolidine*, m.p. 86—87°. Et lactate, $CO(NH_2)_2$, and NaOEt–EtOH give 2 : 4-diketo-5-methyloxazolidine, m.p. 48—50°, b.p. 147—148°/5 mm., identical with the product of Traube *et al.* (A., 1913, i, 901), thus proving the structure of (*A*) (cf. Aspelund, *Acta Acad. Aboensis, Math. Phys.*, 1938, **11**, No. 7; 1939, **11**, No. 14). ε-Methyloctan-*β*-one, b.p. 100—102°/50 mm. (*semicarbazone*, m.p. 128—129°), is prepared from CMe_2Pr^aBr and $CH_2Ac·CO_2Et$. (*A*) are anæsthetic, those with 8—10 C attached at position 5 being equal to dialkylbarbituric acids. Highly branched compounds are convulsant. M.p. are corr. R. S. C.

Piperidine, phthalimidine, and morpholine derivatives.—See B., 1941, II, 407.

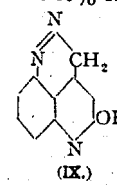
Thiazoles.—See B., 1941, II, 374.

Mercaptothiazoles : oxidation and alkylation studies. E. R. Buchman, A. O. Reims, and H. Sargent (*J. Org. Chem.*, 1941, **6**, 764—773).—2-*Thiol*-4-*methylthiazole* (I), b.p. ~188°/3 mm., m.p. 88·0—88·5°, is obtained by the gradual addition of COMe·CH_2Cl to a well-stirred, ice-cold suspension of $NH_2·CS_2NH_4$ in abs. EtOH, with subsequent keeping at room temp. followed by heating at 100°. 2-*Thiol*-4 : 5-*dimethylthiazole* (II), m.p. 163·5—163·8°, is obtained analogously from COMe·CHMeCl or COMe·CHMeBr and 2-*thiol*-4-*ethylthiazole* (III), m.p. 87·0—87·1°, from COEt·CH_2Br. Slow addition of 30% H_2O_2 to a suspension of (I) in H_2O at 65—70° followed by heating at 80° gives 4-methylthiazole, b.p. 70—71°/59 mm. (picrate, m.p. 181°), and, mainly, the *disulphide*, m.p. 61·0—61·5°, which decomposes on long keeping and cannot be prepared from thiuram disulphide and COMe·CH_2Cl in EtOH. Oxidation of (II) by H_2O_2 in neutral solution yields mainly the corresponding *disulphide* (IV), m.p. 51·6—52°, and some 4 : 5-*dimethylthiazole* (V), b.p. 81—83°/59 mm. [*picrate*, m.p. 186—187°; *methiodide*, m.p. 223—223·5° (decomp.)], also obtained from COMe·CHMeCl and HCS·NH_2 in EtOH at 0—4° and subsequently at room temp. In moderately acid solution the relative proportion of (IV) is diminished and that of (V) is increased whilst in more strongly acid solution (IV) is not obtained and (V) is accompanied by the *thiazole monosulphide*, m.p. 41·0—41·2°, b.p. ~190—200°/2 mm. (*monopicrate*, m.p. 111·0—111·2°). With dil. HNO_3 at 80° the free base is obtained in 65% yield from (II). 2-*Methylthiol*-4-*methylthiazole*, b.p. 65—68°/3 mm. (*picrate*, m.p. 123·5—123·7°), is obtained from (I) and MeI at room temp. either alone or in presence of Et_2O or from $NH_2·CS_2Me$ and COMe·CH_2Cl in boiling abs. EtOH. 2-*Methylthiol*-4 : 5-*dimethylthiazole*, b.p. 87°/2 mm. (*picrate*, m.p. 134·5—135·5°), is prepared analogously from (II) and 2-*ethylthiol*-4-*methylthiazole* (VI), b.p. 83—84°/4 mm. (*picrate*, m.p. 114—114·5°), from (I) and EtBr at room temp. (I) and $ClCO_2Et$ at room temp. afford 2-*carbethoxythiol*-4-*methylthiazole* (VII), b.p. 123—125°/4 mm., which does not form a stable picrate; if the reaction is effected at 100°, CO_2 is evolved and considerable amounts of (VI) accompanied by 2-thiol-4-methylthiazole (VIII) result. (VII) and gaseous HCl at 100° give (VI). $ClCO_2Et$ and $NH_2·CS_2NH_4$ in abs. EtOH at 0° give S-*carbethoxy dithiocarbamate*, $NH_2CS_2·CO_2Et$ (IX), m.p. 98·9—99·4°; with less careful cooling the product appears to be S-*carbethoxy trithiocyanurate*, m.p. >200°. COMe·CH_2Cl and (VIII) in MeOH or Et_2O afford 2-*acetonylthiol*-4-*methylthiazole*, b.p. ~112—115°/3 mm., m.p. 45·5—46·0° (*hydrochloride*, m.p. 158·5—159°), also obtained from COMe·CH_2Cl and $NH_2·CS_2NH_4$ in boiling anhyd. Et_2O or from (IX) and COMe·CH_2Cl is abs. EtOH. Pure (IV) is unchanged after some months but the crude product, m.p. 48°, under similar conditions is largely decomposed giving (II) and 4 : 5-dimethylthiazole 2-monosulphide. H. W.

Benzthiazyl [furyl] derivatives.—See B., 1941, II, 404.

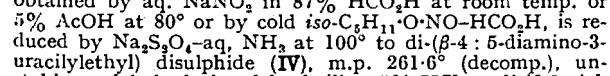
Cyclic aminoalkylamino-derivatives of lepidine. S. E. Krahler and A. Burger (*J. Amer. Chem. Soc.*, 1941, **63**, 2367—2371).—2-Chlorolepidine (I) (prep. in 95% yield from the 2-OH-compound), m.p. 58°, is reduced by H_2–Raney Ni in KOH–EtOH to lepidine (1 atm.; 16 hr.), with 1-*β*-aminoethylmorpholine (II) at 150° gives 1-*β*-2′-lepidylaminoethylmorpholine [*dihydrochloride* (III), m.p. 272—273°], and with piperazine (IV) at 130—140° gives, according to the relative amounts, 1-2′-lepidyl- (V), an oil [*mono*-, m.p. 265—267° (decomp.), and *tri-hydrochloride*, m.p. 285·5—286°], and 1 : 4-*di*-2′-*lepidyl-piperazine*, m.p. 236·5—237° [*dinitrate*, m.p. 183—186° (decomp.)]. Fuming HNO_3 (*d* 1·5) and (V) at 0° or 2-chloro-6-nitrolepidine (VI) and (IV) at 150—160° give 1-6′-*nitro*-2′-*lepidylpiperazine*, m.p. 211·5—212·5°. Fuming HNO_3 and (III) at 0° give 1-*β*-6′-*nitro*-2′-*lepidylethylmorpholine*, m.p. 158—158·5° [*nitrate*, m.p. 216·5—220·5° (decomp.)], also obtained from (I) and (II) and reduced by H_2–Raney Ni in EtOH to 1-*β*-6′-*amino*-2′-*lepidylethylmorpholine*, m.p. 145—145·5°, sublimes at 120°/1 mm. Nitration of (I) gives >10% of (VI) and 66% of 2-*chloro*-5-*nitrolepidine* (VII), m.p.

133—134°. (**VII**) is reduced by H_2–Raney Ni in EtOH to *2-chloro-5-aminolepidine* (**VIII**) (92%), m.p. 102·5—103°, converted (diazo-reaction; CuCl) into 2 : 5-*dichlorolepidine*, m.p. 104·5—105°, sublimes at 100°/1 mm., which in boiling conc. HCl gives *5-chloro-2-hydroxylepidine*, m.p. 213·5—214·5°, sublimes at 200°/1 mm. Hydrolysis of (**VIII**) by boiling conc. HCl gives *5-amino-2-hydroxylepidine*, m.p. 294° (decomp.), sublimes at 230°/1 mm., the diazonium chloride of which in hot 50% H_2SO_4 gives *5-hydroxy-3-pyrido*[4 : 3 : 2-de]*cinnoline* (**IX**), m.p. 235·5—236°. H_2–Raney Ni reduces (**VIII**) in KOH–EtOH to *5-aminolepidine* (61%), m.p. 82·5—83·5°, sublimes at 90°/1 mm. [*hydrochloride*, m.p. 285—289° (decomp.)], converted (Sandmeyer) into *5-chloro-*, m.p. 106·5°, and *5-bromo-lepidine*, m.p. 112·5—113·5°. Hydrolysis of (**VII**) gives *5-nitro-2-hydroxylepidine*, m.p. 197—198°. At 100° (**VII**) and (**II**) give 1-*β*-*5′-nitro-2′-lepidylmorpholine*, m.p. 246—247° (decomp.). At 140—150° (**VII**) and (**IV**) give 1 : 4-*di*-*5′-nitro-2′-lepidylpiperazine*, m.p. 320° (decomp.).


(**IX.**)

R. S. C.

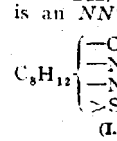
Synthesis of pyrimidine and purine derivatives of cystamine and of a new type of thiazolidinopyrimidine. A. H. Nathan and M. T. Bogert (*J. Amer. Chem. Soc.*, 1941, **63**, 2361—2366).—H_2S and $(CH_2)_2NH$ at ~60° (cooling) give $(NH_2{\cdot}[CH_2]_2)_2S$ (50%), b.p. 130—131°/22 mm. [picrate, m.p. 221—223° (lit. 212°); (*CHPh*:)$_2$, m.p. 56·4—57·4°, and (*CHPh*:*CH*·*CH*:)$_2$ derivative, m.p. 83·5—84°], and $SH{\cdot}[CH_2]_2{\cdot}NH_2$ (**I**) (13·6%). Interaction in the cold (modified) gives 96·7% of (**I**), oxidised by, best, aq. H_2O_2 to $(NH_2{\cdot}[CH_2]_2{\cdot}S{\cdot})_2$ [dihydrochloride, m.p. 217° (lit. 212—215°, 214°); Bz_2 derivative, new m.p. 132·5—133·5°], which with $NH_2{\cdot}CO{\cdot}NH{\cdot}NO_2$ or KCNO–HCl gives 65% of $(NH_2{\cdot}CO{\cdot}NH{\cdot}[CH_2]_2{\cdot}S{\cdot})_2$ (**II**), m.p. 166·5—167·5° [Ac_2, m.p. 208·5—209·5°, and (*CH*$_2$*Cl*·*CO*)$_2$ derivative, m.p. 207·5—208·5°]. $CN{\cdot}CH_2{\cdot}CO_2H$ and (**II**) in warm Ac_2O, exothermally and later at 100°, give *di-(β-cyanoacetylcarbamidoethyl) disulphide* (88·3% crude), m.p. 221—222°, which with cold 30% NaOH, boiling 5% aq. Na_2CO_3, $NaHCO_3$, or (best) NH_3 gives 62—70% of *di-(β-4-imino-3-barbiturylethyl) disulphide* (**III**), m.p. 279° (276°) (decomp.). Hydrolysis of (**III**) by boiling 5% HCl gives di-(*β*-3-barbiturylethyl) disulphide, m.p. 219—220° (lit. 216·8—218·8°), converted by Zn dust in boiling 5% HCl into *thiazolidino-2 : 3-4′ : 3′-* or *-2′ : 3′-barbituric acid* (87·1%), m.p. 300·5—301°. The :N·OH-derivative, $+2H_2O$ [retained at 110°, lost at 150° (decomp.)], m.p. 197—198°, of (**III**) is obtained by aq. $NaNO_2$ in 87% HCO_2H at room temp. or 5% AcOH at 80° or by cold *iso*-$C_5H_{11}{\cdot}O{\cdot}NO$–$HCO_2H$, is reduced by $Na_2S_2O_4$–aq, NH_3 at 100° to di-(*β*-4 : 5-diamino-3-uracilylethyl) disulphide (**IV**), m.p. 261·6° (decomp.), unstable, and is hydrolysed by boiling 5% HCl to *di-(β-3-violurylethyl) disulphide* (**V**), m.p. 230·5—231° (decomp.; pink at ~200°). When heated with $CO(NH_2)_2$ at 170—180°, (**IV**) gives *di-(β-3-uric acid-ethyl) disulphide*, $+H_2O$ (retained at 110°), m.p. >350°. Hydrolysis of (**V**) by HCl and subsequent reduction by Zn–HCl gives *thiazolidinodialuric acid*,



m.p. >330°. M.p. are corr.

R. S. C.

Characterisation of the functional groups of biotin. K. Hofmann, D. B. Melville, and V. du Vigneaud (*J. Biol. Chem.*, 1941, **141**, 207—214).—Biotin (**I**), $[\alpha]_D^{22}$ +92° in 0·1*N*-NaOH, is an *NN′*-disubstituted cyclic urea derivative. (**I**) or its Me ester and aq. $Ba(OH)_2$ at 140° afford a *diaminocarboxylic acid*, $C_9H_{18}O_2N_2S$, decomp. 186—190° [*sulphate*, m.p. 244—255°, $[\alpha]_D^{22}$ −15° in H_2O; Bz_2 derivative, m.p. 182—183° (*Me* ester, m.p. 128—130°)]. (**I**) and H_2O_2–AcOH at room temp. give *biotin sulphone*, $C_{10}H_{18}O_5N_2S$, m.p. 274—275° (decomp.) (*Me* ester, m.p. 239—241°).


(**I.**)

A. T. P.

Phenylthiocarbamides. The triad ·N·C·S·. X. Action of hydrolytic agents, alkaline lead acetate, and nitrous acid on thiosemicarbazide. R. Sahasrabudhey and H. Krall (*J. Indian Chem. Soc.*, 1941, **18**, 225—228).—$NH_2{\cdot}NH{\cdot}CS{\cdot}NH_2$ with N-alkali yields H_2S, NH_3, and HCNS, the primary decomp. being to $NH_2{\cdot}NH{\cdot}CN$, with dil. HCl, small amounts of N_2H_4 and HCNS, with alkaline $Pb(OAc)_2$, $NH_2{\cdot}NH{\cdot}CN$ [*picrate*, $(NH_2{\cdot}NH{\cdot}CN)_2{\cdot}C_6H_2(NO_2)_3{\cdot}OH$, m.p. 272°], and with HNO_2, 5-aminothio-2 : 3 : 4-triazole and (if 2 mols. of HNO_2 are used) NO (20) + N_2 (80%).

A. Li.

VII.—ALKALOIDS.

Isolation of toxic principle from seeds of *Macrozamia spiralis*. J. M. Cooper (*J. Proc. Roy. Soc. New South Wales*, 1940, **74**, 450—454).—*Macrozamin*, $C_6H_{11-13}O_5N$, decomp. 199° (darkens at 196°), from the aq. extract of the seeds of *M. spiralis*, can be acetylated and benzoylatcd, gives Molisch's carbohydrate test, yields HCN on hydrolysis (NaOH) and acidification, and after hydrolysis (HCl) yields an osazone. Given orally (not subcutaneously) it is toxic to guinea-pigs.

A. Li.

Hess synthesis of arecaidine and arecoline. N. A. Preobrashenski and L. B. Fischer (*J. Gen. Chem. Russ.*, 1941, **11**, 140—142).—A repetition of Hess and Leibbrandt's work (A., 1918, i, 401) shows that the substance claimed by these authors as arecoline is in reality unchanged Me *N*-methylhexahydronicotinate, whilst their "arecaidine hydrobromide" (**I**) is in reality the hydrobromide of *N*-methylhexahydronicotinic acid. (**I**), prepared by hydrolysis of arecoline with HBr, has m.p. 242—243°.

R. T.

Alkaloids of *Arthrophytum leptocladum*, M. Pop., of the Chenopodiaceæ family. II. N. K. Juraschevski (*J. Gen. Chem. Russ.*, 1941, **11**, 157—162).—The dried leaves contain leptocladine (**I**) 0·6, dipterine (**II**) 0·7, and an unidentified liquid alkaloid 0·07%, in addition to the substance of m.p. 235—236°, described in Part I (A., 1939, II, 456), now identified as allantoin. (**I**) is identified as 3 : 4-dimethyl-3 : 4 : 5 : 6-tetrahydro-4-carboline, and is synthesised by condensation of (**II**) with MeCHO in dil. H_2SO_4 (20 min. at 110°).

R. T.

Synthesis of *dl*-pelletierine derivatives. M. A. Spielman, S. Swadesh, and C. W. Mortenson (*J. Org. Chem.*, 1941, **6**, 780—785).—dl-*β*-2-*Piperidylpropaldehyde Et*$_2$ *acetal* (**I**) (*pelletierine acetal*) has been used as initial material in the prep. of *dl*-pelletierine derivatives. Although the free alkaloid (**II**) has not been obtained from any of these compounds, a comparison of the synthetic materials with those derived from (**II**) indicates the correctness of the structure assigned to (**II**) by Hess (A., 1917, i, 350). Rapid successive additions of 2-methylpyridine and $CH_2Br{\cdot}CH(OEt)_2$ to LiBu$^\alpha$ in abs. Et_2O at room temp. give *β-2-pyridylpropaldehyde Et*$_2$ *acetal*, b.p. 128°/8 mm. [oxidised to *β*-2-pyridylpropionic acid, m.p. 139—140° (aurichloride, m.p. 162—163°)], accompanied by some *β-2-pyridylheptaldehyde Et*$_2$ *acetal*, b.p. 156—159°/8 mm., or *β-2-pyridylhexaldehyde Et*$_2$ *acetal*, b.p. 145—148°/8 mm., if LiPr$^\alpha$ is used as condensing agent. Hydrogenation (Raney Ni in EtOH) of (**III**) yields (**I**), b.p. 91—92°/1 mm., the N-*Bz* derivative, b.p. 177—178°/1 mm., of which is hydrolysed by 95% AcOH at 90° to 1-benzoylpelletierine, m.p. 74—76° (lit. m.p. 75°). Similarly the N-*Ac* compound of (**I**), b.p. 147—149°/2 mm., is hydrolysed to 1-acetylpelletierine, b.p. 139—141°/2 mm., 174°/18 mm. (aurichloride, m.p. 94°), which instantly reduces Tollens' reagent. Dropwise addition of $ClCO_2Et$ to (**I**) and 30% NaOH affords *β-1-carbethoxy-2-piperidylpropaldehyde Et*$_2$ *acetal*, b.p. 146—147°/2 mm., hydrolysed by 95% AcOH at 90° to the aldehyde, b.p. 119—121°/1 mm. 1-$C_{10}H_7{\cdot}NCO$ and (**I**) in light petroleum afford the very characteristic dl-*β*-1-*α-naphthylcarbamyl-2-piperidylpropaldehyde Et*$_2$ *acetal*, m.p. 109°. (**I**) and boiling Ac_2O give 1-*acetyl-2-γ-ethoxy-Δ*$^{\beta}$*-propenylpiperidine*, b.p. 155—157°/6 mm., which rapidly decomposes cold $KMnO_4$ and decolorises Br in CCl_4.

H. W.

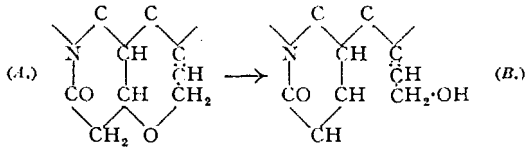
Isolation of ecgonidine methyl ester from coca seeds. J. R. Matchett and J. Levine (*J. Amer. Chem. Soc.*, 1941, **63**, 2444—2446).—Seeds of *Erythroxylon coca*, Lam., and *E. novogranatense* (Morris), Hieron, yield, as sole alkaloid, ecgonidine Me ester (0·03%), $[\alpha]^{21}$ −47·2° in EtOH (*aurichloride*, m.p. 152—153°), hydrolysed to ecgonidine by 5% HCl and prepared therefrom by H_2SO_4–MeOH (the Et ester is similarly prepared).

R. S. C.

Synthesis of vinyl-free cinchona alkaloids and antimalarial activity. V. Prelog, P. Stern, R. Sieweth, and S. Heimbach-Jubász (*Naturwiss.*, 1940, **28**, 750).—6′-Methoxy-9-rubanone has m.p. 90—91° (mono-picrate, m.p. 211—211·5°, and -picrolonate, m.p. 226°) (cf. Rabe *et al.*, A., 1922, i, 361). Catalytic reduction by H_2–PtO_2–EtOH affords 6′-methoxy-9-rubanol, stereoisomerides (*picrate*, m.p. 218°); the hydrochloride has antimalarial activity similar to that of quinine, in spite of the absence of the 3-Et or -CH:CH$_2$ group, which are thus not essential.

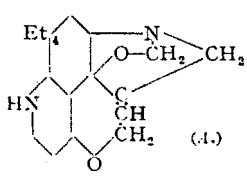
A. T. P.

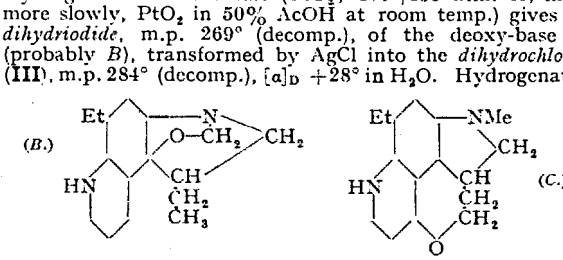
Strychnos **alkaloids. XXV. Behaviour of *Strychnos* alkaloids towards hydrogen bromide.** H. Wieland and R. G. Jennen [with, in part, O. Müller] (*Annalen*, 1940, **545**, 99—112; cf. A., 1929, 708).—Dihydrovomicine (**I**) is readily converted by boiling AcOH–HBr (*d* 1·78) containing red P into *bromodihydrodeoxyvomicine*, $C_{22}H_{25}O_3N_2Br$, m.p. 243° (decomp.) [*hydrobromide* (**II**) decomp. 258°], whereas vomicine (**III**) under these conditions is isomerised to *isovomicine* (**IV**), m.p. 256°, $[\alpha]_D$ +260·3° in $CHCl_3$. (**I**) is transformed by Zn dust in boiling MeOH–AcOH into dihydrodeoxyvomicine (**V**), m.p. 210° (*hydrobromide*, decomp. >290° after becoming brown at 260°). (**I**) is unchanged by 38% HCl at 150°. (**V**) and MeI in MeOH at 100° afford the *methiodide*, m.p. 272° (slight decomp.), reconverted into (**V**), by Na–Hg in warm H_2O. NaOMe in boiling MeOH transforms (**II**) into *iso-dihydrovomicine*, m.p. 185°, which re-forms (**II**) under the action of red P in boiling AcOH–HBr. Dihydrovomicinium methobromide is transformed by red P, fuming HBr, and AcOH into the *hydrobromide* of the deoxy-base, $[C_{23}H_{29}O_3N_2Br]Br$, m.p. 272° (decomp.), debrominated by Zn dust in boiling AcOH–MeOH to *dihydrodeoxyvomicine methobromide*, m.p. 276° (decomp.). Under similar conditions vomicinium methobromide gives a 50% yield of the *hydrobromide* of the corresponding quaternary Br-base, m.p. >300°, debrominated to the very hygroscopic *hydrobromide*, $C_{23}H_{27}O_3N_2Br$, m.p. 206°. Under these conditions (**III**) and strychnine (**VI**) afford the isomeric alkaloids. Dihydrostrychnine, fuming HBr, AcOH, and red P yield *bromodihydrodeoxystrychnine*, $C_{21}H_{23}ON_2Br$, decomp. 280°, debrominated (Zn dust in boiling MeOH–AcOH or H_2–PtO_2 in EtOH) to *dihydrodeoxystrychnine*, m.p. 180°, which is indifferent towards catalytic hydrogenation. Dehydrobrucine and fuming HBr give *bisdemethylbromodihydrodeoxybrucine hydrobromide*, m.p. 268° (decomp.) (also + $2H_2O$), which gives an intense red colour with CrO_3, $FeCl_3$, H_2O_2, and HOCl, does not contain OMe, and is debrominated to bisdemethyldihydrodeoxybrucine (*hydrobromide*, m.p. >295°). (**VI**) and fuming HBr afford *iso*strychnine (**VII**), m.p. 225°, $[\alpha]_D$ +5·23° in



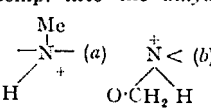
EtOH. The relationship between (**III**) and (**IV**) and between (**VI**) and (**VII**) is the transition (*A*) → (*B*). H. W.

Strychnos **alkaloids. XXVI. Base $C_{16}H_{24}O_2N_2$.** H. Wieland and L. Horner (*Annalen*, 1940, **545**, 112—123; cf. A., 1937, II, 217).—The constitution (*A*) is ascribed to the base $C_{16}H_{24}O_2N_2$ [(**I**), *loc. cit.*] in which the position of Et at $C_{(4)}$ is not firmly established and the possibility of 2 Me in place of Et is not rigidly excluded. Treatment of the corresponding H_2-base (**II**) with boiling, fuming HI in presence of yellow P gives the *hydriodide* of an I-base, m.p. 285° (decomp.); the free base could not be obtained cryst. or de-iodinated by Zn dust and AcOH. Hydrogenation of the salt (PtO_2; 170°/135 atm. or, much more slowly, PtO_2 in 50% AcOH at room temp.) gives the *dihydriodide*, m.p. 269° (decomp.), of the deoxy-base (**I**) (probably *B*), transformed by AgCl into the *dihydrochloride* (**III**), m.p. 284° (decomp.), $[\alpha]_D$ +28° in H_2O. Hydrogenation





(PtO_2 in H_2O) of (**II**) gives the non-cryst. deoxy-base (probably *C*), isolated as the *dihydrochloride* (**IV**), m.p. 300° (decomp.), $[\alpha]_D$ +31° in EtOH. (**III**) and (**IV**) differ markedly from one another in temp. of decomp. and solubility in EtOH. (**IV**) is very hygroscopic whereas (**III**) is stable in air. The *picrates* corresponding with (**III**) and (**IV**) have decomp. 198° and are non-cryst. respectively. (**II**) is reduced by Na and amyl alcohol at 100° to the *base*, $C_{16}H_{28}O_2N_2$, m.p. 172° (opening of one of the oxide rings); it is unaffected by boiling Ac_2O whereas the Zerevitinov determination shows the presence of 2 active H. Dehydrogenation (Pd-black at 230°) of (**I**) gives vomipyrine (**V**), m.p. 105°, and a *base*, $C_{16}H_{18}ON_2$, m.p. 157° (yellow *hydrochloride*), dehydrogenated (Pd at 250°) to (**V**). (**I**) in Et_2O is slowly transformed by MeI at room temp. into the *dihydriodide*, m.p. 235° (decomp.), of the *ditert.* base with the annexed groups; removal of I by TlOH leads to a non-cryst. base which can be distilled unchanged in a high vac. and is extracted from H_2O by $CHCl_3$. The additive compound described previously (*loc. cit.*) from (**I**) and MeI in boiling MeOH has m.p. 259° (decomp.) and is now shown to be a methiodide (*a*)–hydriodide (*b*). Treatment of this salt with Ag_2O and distillation of the free base in a high vac. leads to a non-cryst. material, transformed by treatment with MeI in Et_2O into the *dihydriodide*, $C_{19}H_{32}O_2N_2I_2$, m.p. 224° (decomp.); this with TlOEt yields NMe. Addition of MeI to the *tert.*-*N*-Me base yields a basic methiodide, transformed by HI into a *dihydriodide*, $C_{18}H_{30}O_2N_2I_2$, decomp. ~244° after darkening at 190°. (**II**) is converted by a large excess of MeI in boiling MeOH into the *dimethiodide*, $C_{19}H_{34}O_2N_2I_2$, m.p. 277°. Oxidation of (**I**) by N-$KMnO_4$ in 20% H_2SO_4 at 0° gives an NH_2-*acid*, $C_{14}H_{20}O_4N_2$, decomp. 245° after becoming brown [*Me* ester, n.p. 230° (decomp.)], which with fuming HI and P in boiling AcOH yields a *dihydriodide*, $C_{11}H_{22}O_2N_2,2HI$, m.p. 232° (decomp.). H. W.



Veratrine alkaloids. XI. Dehydrogenation of jervine. W. A. Jacobs, L. C. Craig, and G. I. Lavin (*J. Biol. Chem.*, 1941, **141**, 51—66; cf. A., 1941, II, 272).—Jervine and Se (in N_2) at 340° afford 5-methyl-2-ethylpyridine, possibly 3-hydroxy-5-methyl-2-ethylpyridine, m.p. 145—147°, and a trace of compound, $C_{20}H_{22}O$, m.p. 141—145°, together with the hydrocarbons, $C_{14}H_{14}$, an oil (picrate, m.p. 87—89°) (possibly a methyl-4 : 5-benzohydrindene), $C_{20}H_{22}$, m.p. 73—79°, $C_{26}H_{16}$, m.p. 125—127°, $C_{21}H_{24}$, m.p. 70—81°, $C_{24}H_{30}$, m.p. 100—101°, $C_{22}H_{20}$, m.p. 154—155°, and (?) $C_{41}H_{18}$, m.p. ~145—150°. A. T. P.

Veratrine alkaloids. XII. Further studies on the oxidation of cevine. L. C. Craig and W. A. Jacobs (*J. Biol. Chem.*, 1941, **141**, 253—267; cf. A., 1940, II, 316).—Cevine is oxidised (*loc. cit.*) and the products are methylated (CH_2N_2) to give the *Me*$_4$ ester (**I**), m.p. 65—66°, $[\alpha]_D^{25}$ +22° in MeOH, of a *hexanetetracarboxylic acid*, $CO_2Me{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2Me$, the *Me*$_2$ ester of an acid, $C_{11}H_{14}O_8$ or $C_{11}H_{16}O_8$, the *Me*$_2$ ester of a (?) *heptanetetracarboxylic acid* (corresponding *acid*, $C_{11}H_{16}O_8$, m.p. 145—148°), and a *Me*$_3$ ester, $C_{17}H_{24}O_8$ [hydrolysed to an acid (**II**) $C_{14}H_{18}O_8$, which is the precursor of decevinic acid, $C_{14}H_{14}O_6$, m.p. 275—278° (structure obscure), obtained on heating (**II**) at 200° in N_2, when it loses 2 H_2O], together with a (?) methylpyrrolidone, C_5H_9ON, m.p. 58°, and a (?) methylpiperidone, $C_6H_{11}ON$, m.p. 34—37°. (**I**) and excess of N-NaOH at 100° (bath) give the corresponding *tetracarboxylic acid*, m.p. 170—175°, converted by distilling at 230°/0·2 mm. into the *dianhydride* (**III**), $C_{10}H_{10}O_6$, m.p. 154—160° (effervescence), $[\alpha]_{11}^{25}$ +67° in $COMe_2$, and, after redistilling the residues from (**III**) at 250°/10 mm., the *ketomonoanhydride*, $C_9H_{10}O_4$, m.p. 115—118°, $[\alpha]_D^{25}$ +128° in $COMe_2$. A. T. P.

Aconite alkaloids. VII. Staphisine, a new alkaloid from *Delphinium staphisagria*. W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1941, **141**, 67—84; cf. A., 1941, II, 55).—Delphinine mother-liquors from *D. staphisagria* afford (chromatographic analysis) *staphisine* (**I**), (?) $C_{22}H_{31}ON$ (contains NMe but not OMe), m.p. 205—208° (softens at 195° after sintering from 170°), $[\alpha]_D^{25}$ −159° in C_6H_6 (*hydrochloride*, softens at 248°, decomp. at 256°; *hydrobromide*, softens to a resin at 255—258°; *nitrate*, resin at 236—243°); it possibly contains a little of an ether or anhydro-compound, $C_{44}H_{60}ON_2$. Hydrogenation [PtO_2–MeOH(+HCl); 3 atm.] affords a little of a product, $C_{44}H_{64}ON_2$, m.p. varies from 205—209° to 252—254°. With MeI at 100° (**I**) gives probably $C_{44}H_{60}ON_2$,MeI, softens at 245°, effervesces at 255°, further methylated to (?) $C_{22}H_{31}ON$,MeI, softens at >240°, effervesces at 250°. Dehydrogenation of (**I**) with Se (in N_2) at 340° affords the *hydrocarbons*, $C_{16}H_{14}$, m.p. 78—81° (sinters at

73°) (*picrate*, m.p. 129—131°), $C_{18}H_{18}$, m.p. 55—63° (*picrate*, m.p. 153—155°), probably di- and tetra-methylphenanthrenes, respectively); $C_{18}H_{18}$ or $C_{19}H_{20}$, m.p. 53—57° (*picrate*, m.p. 142—144°) [(?) tetra- or penta-methylphenanthrene], $C_{19}H_{20}$, m.p. 73—75° (*picrate*, m.p. 143—144°) (pentamethyl-), $C_{20}H_{22}$ [(?) hexamethyl-] (*picrate*, m.p. 235—137°), and a (?) hepta-methylphenanthrene. In addition to (**I**), a trace of alkaloid, m.p. 300° (decomp.), is also isolated. A. T. P.

VIII.—ORGANO-METALLIC COMPOUNDS.

Organic arsenicals in peace and war. G. J. Burrows (*J. Proc. Roy. Soc. New South Wales*, 1940, **74**, M1—M16).—The prep., properties, and applications of org. arsenicals are reviewed. A. Li.

Arsenobenzenes.—See B., 1941, III, 346.

Mercury diallyl and mercuric allyl halides. K. V. Vijayaraghavan (*J. Indian Chem. Soc.*, 1940, **17**, 589—592).—Hg^{II} allyl iodide is reduced (alkaline Na stannite) to *Hg diallyl*, which rapidly decomposes to Hg and diallyl. With ethereal Br it gives *Hg^{II} allyl bromide*, m.p. 124—125° (decomp.), and with Cl_2–CCl_4 gives the *chloride*, m.p. 102—103° (decomp.). F. R. S.

Relative reactivities of organo-metallic compounds. XLI. Lithium *sec.*- and *tert.*-alkyl compounds. Interconversion reactions with them. H. Gilman, F. W. Moore, and O. Baine. **XLII. Preferential cleavage of radicals in organo-metallic compounds.** H. Gilman, F. W. Moore, and R. G. Jones (*J. Amer. Chem. Soc.*, 1941, **63**, 2479—2482, 2482—2485).—XLI. In light petroleum (**I**) (free from unsaturated compounds), b.p. 28—38°, RCl, and Li give 85% yields of LiR (R = Bu^a, Bu$^\beta$, CHMeEt, *n*-amyl, Pr^a; 50% if R = Bu$^\gamma$; 75% if R = Pr$^\beta$). RBr gives lower yields. For metallation of dibenzfuran (**II**) the order of efficiency of LiR in Et_2O is R = Bu^a > Bu$^\beta$, Et > *n*-amyl > Ph > Me and in (**I**) is R = Bu$^\gamma$ > CHMeEt, Pr$^\beta$ > Bu^a, Bu$^\beta$; LiBu^a is more effective in Bu^a_2O than in Et_2O. Aromatic solvents cannot be used owing to slow reaction of (**II**) and their own metallation; *e.g.*, LiCHMeEt in PhMe gives 8% of $LiCH_2Ph$. *p*-C_6H_4MeNa or $NaCH_2Ph$ and (**II**) in C_6H_6 or PhMe give 60—80% of 4 : 6-Na_2 derivative, but KCH_2Ph is ineffective. For the reaction, α-$C_{10}H_7Br$ + LiR → α-$C_{10}H_7Li$ + RBr, in (**I**) the order of efficiency is R = CHMeEt > Pr$^\beta$ > Bu$^\gamma$ > Bu^a, Bu$^\beta$ > Pr^a (cf. the order in Et_2O; A., 1940, II, 334); in Et_2O *n*-$C_5H_{11}Li$ is less effective than LiBu^a; in (**I**) LiBu^a is superior to NaBu^a. For addition of LiR to CH_2:CPh_2 in (**I**) or C_6H_6–(**I**) the (approx.) order is R = CHMeEt > Bu$^\beta$ > Bu^a > Bu$^\gamma$.

XLII. Metallation of Ph in $PbPhR_3$ by interaction of LiR′ therewith or with *p*-C_6H_4Br·PbR_3 is impossible owing to cleavage of the Pb-aryl linking (giving LiAryl). 4 : 2 : 1-NO_2·C_6H_3I·OMe and $SnCl_2$ in 95% EtOH give 70% of 4 : 3 : 1-OMe·C_6H_3I·NH_2, which affords (diazo-reaction; *diazonium mercurichloride*, decomp. 145°) *Hg di-3-iodo-4-methoxyphenyl*, m.p. 253—254°, which with LiBu^a in Et_2O and later CO_2 gives a small amount of Hg-containing acid, m.p. 250—260°, and much metal–metal interconversion. Interaction of $PbPh_2(C_6H_4Cl$-*p*$)_2$ and LiBu^a gives 98% of *p*-C_6H_4ClLi and 2% of LiPh. Cleavage by LiBu^a under comparable conditions is $PbPh_4$ 30, $SnPh_4$ 45, and $Pb(C_6H_4Me$-*o*$)_4$ 3%. The relative ease of cleavage of $PbPh_4$ by LiR is R = Et > Pr^a > Bu^a > Me > C≡CPh and for $Sn(C_6H_4Cl$-*p*$)_4$ in Et_2O is Bu^a > Bu$^\beta$ > CHMeEt > Bu$^\gamma$ (nil). R. S. C.

Reaction of rhenium trichloride with magnesium methyl iodide. H. Gilman, R. G. Jones, F. W. Moore, and M. J. Kolbezen (*J. Amer. Chem. Soc.*, 1941, **63**, 2525—2526).—Contrary to previous statements (A., 1939, II, 253), $ReCl_3$ and MgMeI give only CH_4 and C_2H_6 (in one case 91·4%), possibly owing to undetectable impurities. $ReCl_3$ catalyses interaction of MgMeI with MeI. R. S. C.

IX.—PROTEINS.

Occurrence of *d*-amino-acids in gramicidin and tyrocidine. F. Lipmann, R. D. Hotchkiss, and R. J. Dubos (*J. Biol. Chem.*, 1941, **141**, 163—169; cf. A., 1940, III, 352).—Enzymic assay with *d*-amino-acid oxidase shows that of the α-NH_2-acids of gramicidin or tyrocidine hydrolysates, 45 or 20%, respectively, have the *d*-configuration. A. T. P.

Chemical nature of gramicidin and tyrocidine. R. D. Hotchkiss (*J. Biol. Chem.*, 1941, **141**, 171—185; cf. A., 1940, III, 352).—Gramicidin (**I**) is a polypeptide (14·8% N), with no free NH_2 or CO_2H. The total N content of the acid hydrolysate is accounted for by *l*-tryptophan (**II**) (37·3%), other α-NH_2-acids (53·9%), additional primary NH_2-compound (7·8%), and NH_3 (1·4%); (**II**), *d*-leucine (**III**), and alanine (**IV**) are isolated. (**I**) may be $C_{74}H_{105}O_{13}N_{15}$, consisting of 3 groups of (**II**) and 9 other NH_2-acids, of which some are (**III**) and (**IV**), and one is a 1 : 2-aminohydroxy-acid (not an α-NH_2-acid). Tyrocidine (**V**), (?) $C_{63}H_{83}O_{13}N_{13}$, and HCl–AcOH give a hydrolysate affording tyrosine, dibasic NH_2-acid (in part, aspartic acid), and tryptophan, and (**V**) appears to be a polypeptide of ~20 NH_2-acid residues combined such that 2 basic NH_2, 3 amide, and 1 CO_2H or acidic OH are free. A. T. P.

Composition of gramicidin and tyrocidine. H. N. Christensen, R. R. Edwards, and H. D. Piersma (*J. Biol. Chem.*, 1941, **141**, 187—195; cf. preceding abstract).—Gramicidin is a polypeptide including among its components *l*-tryptophan, *d*-leucine, and a hydroxyamino-compound, and tyrocidine (min. mol. wt. = 2700) is a polypeptide containing tryptophan, tyrosine, alanine, phenylalanine, a dicarboxylic amino-acid, NH_3, and nitrogenous bases pptd. by phosphotungstic acid. A. T. P.

Properties of gramicidin. M. Tischler, J. L. Stokes, N. R. Trenner, and J. B. Conn (*J. Biol. Chem.*, 1941, **141**, 197—206).—Gramicidin (**I**) is a single substance, but retains 2% of H_2O tenaciously; it can be obtained from tyrothricin by prolonged Et_2O extraction, and has m.p. 228—230°. Its *flavianate* (**II**), decomp. 215—218°, is a complex readily dissociated in MeOH; (**I**) also forms a cryst. rufianate. The mol. wt. of (**I**) appears to depend on the nature of the solvent and concn. of solute; in *cyclo*hexanone, vals. of 600—1200 are obtained. Isothermal distillation gives a val. of 3100. The mol. wt. of (**II**) indicates a val. of 300 for (**I**). A. T. P.

Thiol groups of ovalbumin in different denaturing agents.—See A., 1941, III, 1060.

Nitrosobenzene-hæmoglobin. F. Jung (*Naturwiss.*, 1940, **28**, 264—265).—PhNO forms a mol. compound with hæmoglobin (**I**). It is violet, like reduced (**I**), and has a wide absorption band like the latter, but with two flat max. at 567 and 543 mμ. It is obtained by the action of NH_2Ph on methæmoglobin (**II**), or from oxy- or carboxy-hæmoglobin. By the action of reducing agents of the type and concn. found in fresh blood corpuscles the compound is rapidly converted into (**II**). NHPh·OH is formed intermediately and gives PhNO with atm. O_2. Owing to the presence in the blood of reducing agents such as ascorbic acid, NHPh·OH or NH_2Ph in the body can convert many times its own no. of mols. of (**I**) into (**II**) in a short time. *m*-C_6H_4Me·NO and *m*-NO_2·C_6H_4·NO behave in the same way as PhNO towards (**I**), but *p*-NO·C_6H_4·NMe_2 and *p*-OH·C_6H_4·NO do not, probably because of their quinonoid structure. A. J. M.

Addition reaction of alkali-treated silk.—See A., 1942, II, 5.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Lignin and related compounds. LIII. Isolation of vanilloyl and syringoyl methyl ketones from ethanolysis products of maple wood. M. Kulka, W. L. Hawkins, and H. Hibbert (*J. Amer. Chem. Soc.*, 1941, **63**, 2371—2374; cf. A., 1941, II, 371).—Mixed syringoyl (**I**) and vanilloyl Me ketone (**II**) are isolated from the $NaHSO_3$-sol. portion of the ethanolysis products of maple wood by heating with aq. NH_2OH,H_2SO_4, $NiCl_2$, and NaOAc in CO_2 and decomp. the resulting Ni dioximes by 12N-H_2SO_4 at room temp. (later 40°). (**I**) and (**II**) are then separated by means of the NH_4 salt of (**I**). The amounts of (**I**) and (**II**) thus obtained are 2—3% of the Klason lignin. α-Hydroxypropiosyringone and $CuSO_4$ in 1 : 2 H_2O–C_5H_5N at 100° give (**I**), m.p. 80—81°, b.p. 147°/0·04 mm. [*semicarbazone*, m.p. 210—211° (decomp.); *quinoxaline* derivative, m.p. 161—161·5°]. R. S. C.

Bitter principles of *Citrus decumana*. (Miss) A. Mookerjee (*J. Indian Chem. Soc.*, 1940, **17**, 593—600).—From the seeds of *C. decumana*, limonin (**I**), and *neolimonin* (**II**), $C_{26}H_{30}O_8$,2EtOH, m.p. 240—242° (decomp.), $[\alpha]_D^{32}$ −111° in $COMe_2$, have been isolated. (**I**) forms an *Ac* derivative, m.p.

219—220°, and a *phenylhydrazone*, m.p. 215—220°, and with HCl gives hexahydrolimoninic acid, m.p. 201—203° (lit. 178°) (Me ester, m.p. 173—174°), which is also obtained, together with *iso*limonin (**III**), by the action of KOH on (**I**). The colour reactions of (**I**), (**II**), and (**III**) are described.

F. R. S.

African arrow poisons. III. Crystalline *Calotropis* resin. G. Hesse, H. Eilbracht, and F. Reichender (*Annalen*, 1941, **546**, 233—252; cf. A., 1939, II, 81).—The sole alcoholic component is α-lactucerol (**I**), which is purified by fractional crystallisation of the product of hydrolysis, by prep. of the pure benzoate, m.p. 257°, and its hydrolysis, by similar treatment of the acetate, m.p. 252°, or by chromatographic adsorption (Al_2O_3); it then has m.p. 224·5°, $[\alpha]_D$ +97·5° in $CHCl_3$, for the product desiccated at 140° [(**I**) retains solvent of crystallisation very obstinately]. (**I**) is identical with taraxasterol (Burrows *et al.*, A., 1938, II, 80). Attempts to isolate (**I**) by methods involving a pre-purification through the acetate give unsatisfactory results since (**I**) is isomerised by acids to *isolactucerol* (**II**), m.p. 201°, $[\alpha]_D^{20}$ +66·8° in $CHCl_3$ [*acetate*, m.p. 237°; benzoate, m.p. 271° (slight decomp.)], which is probably not identical with β-lactucerol, for which very varied consts. are recorded. O in (**I**) is present in OH since (**I**) is oxidised by CrO_3 to a >CO *compound*, $C_{30}H_{48}O$, m.p. 181° [*oxime*, m.p. 262° (dcomp.)], and further a *substance*, $C_{30}H_{48}O_2$, m.p. 195°, which does not neutralise alkali and is probably a very difficultly hydrolysable lactone. The resistance of the esters to alkali is regarded as evidence of the existence of OH as a primary alcoholic group. (**I**) contains a double linking as shown by the yellow coloration with $C(NO_2)_4$, titration of the esters with Br, and by catalytic hydrogenation, which under varied conditions always leads to a *dihydro-α-lactucerol*, m.p. 216°; this is also obtained from (**II**) so that the isomerisation of (**I**) to (**II**) by acids is a displacement of the double linking. The established composition of (**I**) and (**II**) requires the presence of five hydrogenated C rings as found in amyrin, oleanolic acid, and hederagenin. Dehydrogenation (Se) of (**I**) yields sapotalin, characterised as the picrate, m.p. 130°, and styphnate, m.p. 157°, and a hydrocarbon, $C_{14}H_{16}$, showing that (**I**) belongs to the group of pentacyclic triterpenes. Under milder conditions large proportions of a *hydrocarbon*, $C_{30}H_{52}$, m.p. 230°, are obtained; this does not give a picrate and is saturated towards $C(NO_2)_4$. It is isomeric but not identical with Ruzicka's amyrau, m.p. 228°. A further *hydrocarbon*, m.p. 195—197°, appears to be $C_{13}H_{24}$ and is probably a hydrogenated $C_{10}H_5Me_3$; it does not yield a picrate and is saturated towards $C(NO_2)_4$. Further, a new *isomeride*, m.p. 215°, of (**I**) is described. The crude resin is a mixture of the esters of (**I**) with many fatty acids; from it, the acetate, m.p. 252°, and the iso*valerate*, m.p. 178°, have been obtained pure. Complete separation of the components by crystallisation or chromatographic analysis appears impossible. The main portion of the acids obtained by hydrolysis has b.p. 180—204° and consists of a mixture of $Bu^{\alpha}CO_2H$ and hexoic acid (**III**) from which homogeneous $Bu^{\beta}CO_2H$ can be isolated. (**III**) obstinately retains an unsaturated acid which is separated by chromatography of the vapour and identified as γ-methyl-Δ$^{\beta}$-pentenoic acid, analysed as the dibromide, m.p. 100°. When distilled it gives the lactone, $\begin{matrix}CH_2\text{—}CO\\ CH_2\cdot CMe_2\end{matrix}\!\!>O$, and when ozonised it affords MeCHO. The biogenesis of isoprene compounds is discussed.

H. W.

Chemical composition of *Roccella montagnei*.—See A., 1941, III, 1085.

XI.—ANALYSIS.

Adiabatic fractionating column and precision-spaced wire packing for temperature range −190° to 300°.—See A., 1942, I, 28.

Determination of fluorine in organic compounds. D. H. Brauns (*J. Res. Nat. Bur. Stand.*, 1941, **27**, 105—111).—F in many org. compounds, including some volatile at room temp., can be determined by treatment with H_2SO_4 and KNO_3 in a Pyrex flask, the loss in wt. of which is measured. Apparatus for the purpose and the operation of the method are described in detail, with particular reference to determination of F in $CH_2Bu^{\beta}F$. The glass used is standardised with CaF_2.

J. W. S.

Determination of trichloroethylene. D. F. Kelly, M. O'Connor, and J. Reilly (*Analyst*, 1941, **66**, 489—490).—CCl_2:CHCl (**I**) is quantitatively hydrolysed to KCl by 25% wt./vol. aq. KOH in a sealed Carius tube at 150° for 1 hr. The ratio of KOH to (**I**) by wt. must be 2 or 3 : 1. Lower proportions of KOH and lower temp. of hydrolysis with longer heating times were unsatisfactory. Cl is determined by Volhard's method.

S. T. P. B.

Adsorption analysis. IV. Separation of mixtures of higher saturated fatty acids. H. G. Cassidy (*J. Amer. Chem. Soc.*, 1941, **63**, 2735—2739; cf. A., 1941, II, 210).—Fatty acids are separated by adsorption from low-boiling light petroleum on C and elution by low- or high-boiling light petroleum or C_6H_6 containing 2—4% of MeOH. Separation is followed by the amounts of acid in successive portions of the issuing eluate. Only certain types of C are suitable. *p*-Acylamidoazobenzenes are not separated by chromatography.

R. S. C.

Micro-diffusion methods based on the bisulphite reaction. I. Determination of acetone.—See A., 1942, III, 76.

***o*-Iodosobenzoic acid, a reagent for the determination of cysteine, glutathione, and substituent thiol groups of proteins.** L. Hellerman, F. P. Chinard, and (Miss) P. A. Ramsdell (*J. Amer. Chem. Soc.*, 1941, **63**, 2551—2553).—*o*-$CO_2H\cdot C_6H_4\cdot IO$ (**I**) and mercaptans at 17—22° and p_H 7 give very rapidly disulphides + *o*-$C_6H_4I\cdot CO_2H$ or, if a large excess of (**I**) is used, also sulphinic or sulphonic acids. The former reaction is used to determine cystine (procedure described in detail), glutathione, the SH of ovalbumin and urease. At p_H 7 (**I**) does not react with NH_2-acids.

R. S. C.

Anomalous bromination reaction. Analytical bromination of styrene and indene by the Kaufmann method. C. W. Jordan (*J. Amer. Chem. Soc.*, 1941, **63**, 2687—2689).—Bromination of CHPh:CH_2 or indene by Br–NaBr–MeOH (Kaufmann *et al.*, B., 1925, 302; 1926, 445) is quant. if the consumption of Br is measured, but approx. half the Br is eliminated as HBr, and CHPh:CHBr or CPhBr:CH_2 is formed as well as $CHPhBr\cdot CH_2Br$.

R. S. C.

Determination of dulcin (*p*-phenetylcarbamide). J. F. Hirst, F. Holmes, and G. W. G. Maclennan (*Analyst*, 1941, **66**, 450—451).—Dulcin (**I**) is completely hydrolysed by boiling with 18N-H_2SO_4: consistently high results are obtained. For the semi-micro-determination in beverages alcohol is removed by distillation and essential oils are extracted with light petroleum; (**I**) is then removed by three extractions with EtOAc, the extracts are washed with H_2O, the EtOAc is distilled off, and the residue taken up in COMe. The $COMe_2$ solution is rinsed into a Kjeldahl flask, $COMe_2$ evaporated, and the (**I**) hydrolysed with 18N-H_2SO_4. After boiling for 3 hr. the solution is made alkaline with 30% NaOH and steam-distilled and the NH_3 nesslerised. One commercial sample of (**I**) contained 20% of *p*-diphenetylcarbamide produced by overheating in manufacture.

E. B.

Sulphonamides and the cobalt colour tests for barbiturates. T. Koppanyi, M. W. Green, and C. R. Linegar (*J. Amer. Pharm. Assoc.*, 1941, **30**, 246—247).—Sulphathiazole or sulphapyridine does not interfere with the assay of barbiturate preps. provided that the Dille–Koppanyi procedure (B., 1935, 173) is strictly followed.

F. O. H.

Determination of theobromine and its salts and phenobarbital in mixtures. C. W. Bell (*J. Amer. Pharm. Assoc.*, 1941, **30**, 240—246).—Phenobarbital (**I**) is removed by extraction with Et_2O and residual theobromine (**II**) is determined by treatment with $AgNO_3$, followed by titration of the liberated HNO_3. (**I**) in mixtures of (**I**) and (**II**) is determined by separating (**I**) and titrating (**I**) in 0·4N-NaOH in 50% EtOH with 0·1N-$AgNO_3$. Data for the solubilities of (**I**) and (**II**) in EtOH, C_6H_6, CCl_4, $CHCl_3$, Et_2O, light petroleum, and H_2O are tabulated.

F. O. H.

[Determination of] methylene-blue. H. O. Moraw (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 806—809).—It is recommended that in the official method ("Methods of Analysis," A.O.A.C., 1940, 576) the factor should be 0·006618 g. of anhyd. $C_{16}H_{16}N_3ClS$ = 1 ml. of 0·1N-I; that the first 30 ml. of the filtrate (para. 58) be discarded; and that loss of wt. on drying at 110° for 12—14 hr. be determined (para. 57*a*).

A. A. E.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

FEBRUARY, 1942.

I.—ALIPHATIC.

Polymerisation of hydrocarbons.—See B., 1941, II, 366.

Low-temperature catalytic alkylation of *iso*paraffins. P. D. Caesar and A. W. Francis (*Ind. Eng. Chem.*, 1941, **33**, 1426—1428).—In the low-temp. alkylation of *iso*paraffins by alkenes, whether catalysed by H_2SO_4 or by metal halides, the olefine wedges itself between a Me group and the rest of the *iso*paraffin so that Me adds to one side of the double linking and the *iso*paraffin residue to the other. The Me farthest from the *tert.* C is split off in the case of *iso*-C_5H_{12}. C_2H_4 may behave as CHMe:, and straight-chain butenes may give the same products as does $CMe_2{:}CH_2$ because of the more facile isomerisation of the olefines. In any group of isomeric paraffins so formed, the relative amounts of the isomerides agree closely with those computed by thermodynamic equilibria provided those isomerides are excluded which are not permitted by the proposed mechanism. C. R. H.

Fischer–Tropsch synthesis of hydrocarbons with special reference to its reaction mechanism.—See A., 1942, I, 68.

Photochemical chlorination of methane.—See A., 1942, I, 69.

Iodination. II. Iodination of different unsaturated organic compounds in the dark in different non-polar solvents. J. C. Ghosh, S. K. Battacharyya, M. M. Dutt, and M. J. Rao. **III. Iodination of different unsaturated organic compounds in the dark in polar solvents.** S. K. Battacharyya and M. J. Rao. **IV. Photo-iodination of different unsaturated organic compounds in light of different frequencies in non-polar solvents. V. Photo-iodination of phenylacetylene in light of different frequencies in polar solvents.** S. K. Battacharyya (*J. Indian Chem. Soc.*, 1941, **18**, 245—252, 253—256, 257—268, 269—272).—II. The rate of addition of I to β-amylene (I) and *d*-pinene in the dark in CCl_4, C_6H_6, or CS_2 $\propto$ [acceptor] × $[I]^3$, is little affected by change in temp. or in reaction surface (by addition of quartz sand or beads), and is favoured by $C_6H_6 > CCl_4 > CS_2$. The mechanism $A + I_6 \rightleftharpoons AI_2 + 2I_2$ is suggested.

III. The rate of addition of I to (I) and CPh:CH in EtOH or AcOH in the dark $\propto$ [acceptor]$[I]^2$, has a low temp. coeff., and is greater in EtOH than in AcOH. The mechanism $A + I_4 \rightleftharpoons AI_2 + I_2$ is suggested.

IV. Iodination of CPh:CH (II), dic*yclo*pentadiene (III), $(CH{\cdot}CO_2Me)_2$, (I), and CPh:C·CO_2H in CCl_4 in light of λ 546, 436, and 366 mμ. is reversible and can be explained in terms of chain reactions involving I atoms. The unimol. reaction coeff. $\propto \sqrt{}$(intensity of absorbed radiation), and almost $\propto$ [acceptor]. The quantum efficiency is very high for (II) and (III), low for the rest.

V. Iodination of (II) in EtOH in light of λ 366, 436, and 546 mμ. has been studied with results similar to those in Part IV. Quantum efficiency and temp. coeff. are small. A. Li.

Raman effect. CXVIII. Rotation isomerism. X. Dihalogenoethanes.—See A., 1942, I, 41.

Raman effect. CXVII. Rotation isomerism. IX. Alkyl polyhalides.—See A., 1942, I, 41.

Raman effect. CXIX. Tetrachlorethylene.—See A., 1942, I, 41.

Raman effect. CXX. Rotation isomerism. XI. Halogen-substituted butane.—See A., 1942, I, 41.

Production of polyhydric alcohols.—See B., 1941, II, 367.

Purification of pentaerythritol.—See B., 1941, II, 367.

Separation and identification of fatty acids. VI. Preparation of pure linoleic and linolenic acids by hydroxamic acid method. Y. Inouye and H. Yukawa (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 771—775).—The prep. of linoleic acid from cottonseed and soya-bean oils, and of linolenic acid from linseed oil, is described. 33% of linoleohydroxamic acid is obtained from cottonseed oil, and ~20% from soya-bean oil, whilst 44 g. of linseed oil yield 8·7 g. of linolenohydroxamic acid. J. N. A.

Manufacture of anhydrides of higher fatty acids.—See B., 1941, II, 368.

Reaction of high polymerides in solution. Alkaline saponification of polyvinyl acetate.—See A., 1942, I, 68.

Synthesis of α-keto-β-hydroxybutyric acid. E. Hoff-Jorgensen (*Z. physiol. Chem.*, 1940, **265**, 77—79).—EtCOBr is converted by CuCN at 100° into EtCO·CN, which with Br in AcOH affords CHMeBr·CO·CN, m.p. 111° (2 : 4-*dinitrophenylhydrazone*, m.p. 198°). This is decomposed by strong bases but is transformed by $Pb(OAc)_2$ at 80° into *α-keto-β-hydroxybutyramide* (I), m.p. 212° (2 : 4-*dinitrophenylhydrazone*, m.p. 214°). (I) is hydrolysed and immediately decarboxylated by bases but is converted by 0·5N-HCl at 100° into the non-cryst. very hygroscopic *α-keto-β-hydroxybutyric acid* (very unstable 2 : 4-dinitrophenylhydrazone). H. W.

Michael condensation. VI. Instability of some additive compounds.—See A., 1942, II, 20.

Condensation of heterocyclic amines with dicarboxylic acid anhydrides.—See A., 1942, II, 31.

Formaldehyde: properties, analysis, and manufacture.—See B., 1941, II, 365.

Manufacture of aldehydes.—See B., 1941, II, 370.

Photolysis of acetone in presence of mercury.—See A., 1942, I, 68.

Keten in the Friedel-Crafts reaction. II. Use of mixed acetic anhydrides.—See A., 1942, II, 16.

Volatile alkylamines in human metabolism.—See A., 1942, III, 156.

Preparation of high-mol. wt. primary amines.—See B., 1941, II, 370.

Function of carbonate in the synthesis of glycine from chloroacetic acid, ammonium hydroxide, and ammonium carbonate.—See A., 1942, I, 68.

Cysteinesulphonic acid, m.p. 184—185°.—See A., 1942, III, 147.

Synthesis of aspartic acid. Y. Tsuchiya (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 706—710).—Fumaric acid (1 mol.), NH_3 (2 mols.), and NH_4Cl (4 mols.) at 180°/10 atm. for 1 hr. give aspartic acid in 60—65% yield. J. N. A.

Glabrin, a new component of the seeds of *Pongamia glabra*. N. V. S. Rao and J. V. Rao (*Proc. Indian Acad. Sci.*, 1941, **14**, A, 123—125).—The seeds of *P. glabra* are extracted successively with light petroleum and methylated spirit and karanjin and *glabrin* (I), $C_7H_{14}O_4N$, m.p. 290° (decomp.), $[\alpha]_D$ −56·1°, are isolated from the spirit extract. (I) is acid to phenolphthalein and litmus, freely sol. in aq. acids and alkalis, gives the ninhydrin test, and yields a Cu salt. Titration in presence and absence of CH_2O indicates 580 as min. mol. wt. It is not readily hydrolysed by 20% HCl. (I) is non-toxic to fishes. H. W.

2-Naphthalenesulphonylserine, m.p. 234—235° (corr.), $[\alpha]_D^{28}$ −6·1° in abs. EtOH.—See A., 1941, III, 989.

Methionine and its derivatives. III. Formation of γ-methylthiolpropylamine and γ-methylthiolpropyl alcohol from methionine. Y. Tsuchiya (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 619—622; cf. A., 1942, II, 5).—Decarboxylation of methionine in liquid paraffin at 250° yields 56·7% of $SMe\cdot[CH_2]_3\cdot NH_2$, converted by HNO_2 into the corresponding alcohol (yield 29·4%). J. N. A.

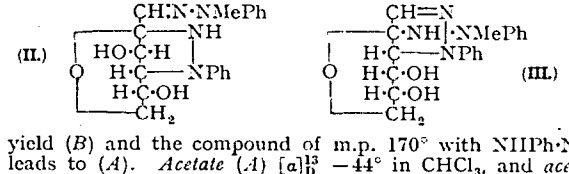
Manufacture of adiponitrile.—See B., 1941, II, 872.

II.—SUGARS AND GLUCOSIDES.

Chemical reactions of the chlorites with carbohydrates. A. Jeanes and H. S. Isbell (*J. Res. Nat. Bur. Stand.*, 1941, **27**, 125—142).—At room temp. and under all conditions which do not involve acid hydrolysis sucrose is unattacked by $NaClO_2$ or $Ca(ClO_2)_2$, whilst ketoses, polyhydric alcohols, and aldonic acids (**I**) are attacked only after treatment for many days. Aldoses (**II**) (*d*-glucose, *l*-arabinose, and lactose), however, are oxidised readily to the corresponding (**I**). Since (**II**) are unattacked by $HClO_3$ or chlorates and only slowly oxidised by ClO_2 it is inferred that the oxidation observed with chlorites is due to free $HClO_2$. J. W. S.

Interaction of aldoses with α-amino-acids or peptides.—See A., 1941, I, 22.

Formation of mixed osazones and their anhydrides. E. E. Percival and E. G. V. Percival (*J.C.S.*, 1941, 750—755).—Galactosephenylmethylhydrazone and $NHPh\cdot NH_2$ give *galactosephenylmethyl-phenylosazone* (**I**), m.p. 178°, $[\alpha]_D^{17}$ +98° in C_5H_5N–EtOH, the *tetra-acetate*, m.p. 183°, $[\alpha]_D^{13}$ +85° in $CHCl_3$, of which is deacetylated ($NaOH$–$COMe_2$) to *anhydrogalactosephenylmethyl-phenylosazone* (**II**), m.p. 172°, $[\alpha]_D^{13}$ +100° in $COMe_2$ (*diacetate*, m.p. 170°, $[\alpha]_D^{15}$ +50° in $CHCl_3$). *p*-$C_6H_4Me\cdot SO_2Cl$ and (**II**) afford *anhydrogalactosephenylmethyl-phenylosazone di-p-toluenesulphonate*, m.p. 65—70° (decomp.), $[\alpha]_D^{15}$ +37° in $CHCl_3$, which does not react with NaI in $COMe_2$. The structure (**II**) is suggested. Attempts to prepare galactosephenyl-phenylmethylosazone give galactosephenylmethylhydrazone (70% yield) with (**I**) (12%). Glucosephenylmethylhydrazone and $NHPh\cdot NH_2$ afford the -osazone (*B*) (cf. Votoček and Vondráček, A., 1904, i, 1055), whilst glucosephenylhydrazone and $NHPh\cdot NHMe$ give (*B*), m.p. 203°, $[\alpha]_D^{17}$ −60° → −15°, and (*A*), m.p. 194°, $[\alpha]_D^{17}$ −53° → −6°. Ofner's fructosephenylmethylhydrazone and $NHPh\cdot NH_2$



yield (*B*) and the compound of m.p. 170° with $NHPh\cdot NH_2$ leads to (*A*). *Acetate* (*A*) $[\alpha]_D^{13}$ −44° in $CHCl_3$, and *acetate* (*B*), $[\alpha]_D^{15}$ −43° in $CHCl_3$, give the same *anhydride* (**III**), m.p. 176—178°, $[\alpha]_D^{13}$ −158° in $COMe_2$ (*diacetate*, m.p. 158°, $[\alpha]_D^{15}$ −151° in $CHCl_3$; *CMe_2* derivative, m.p. 160°, $[\alpha]_D^{18}$ −33° in $COMe_2$), the (p-$C_6H_4Me\cdot SO_2$)$_2$ derivative, m.p. 65—70° (decomp.), $[\alpha]_D^{15}$ −80° in $CHCl_3$, of which does not react with NaI–$COMe_2$. The conclusion reached is that both (*A*) and (*B*) are glucosephenyl-phenylmethylosazones and structure (**III**) is assigned. Possible explanations of the structural differences between two isomeric fructose phenylmethylphenylosazones are considered. F. R. S.

Constitution of new disaccharide produced from starch, and its relation to structure of starch molecule. Y. Nakamura (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 603—612).—Hydrolysis of starch with diastase yields a disaccharide, "*amylolyose*" (osazone, m.p. 160—162°, $[\alpha]_D^{15}$ +59·28° → +46·39° in MeOH), which is 3-[α-*d*-glucosido<1 : 5>]-*d*-glucose<1 : 5>. It is concluded that the starch mol. consists mainly of 1 : 4 units which are united by 1 : 3 and 1 : 6 units. J. N. A.

Components of bark of *Rhamnus japonica*. V. Position of free hydroxyl group of α-sorinin. Z. Nikuni (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 779—783; cf. A., 1940, II, 130).—Methylation (CH_2N_2) of α-sorinin [the primveroside of α-sorigenin (**I**)] followed by hydrolysis with dil. H_2SO_4 yields α-sorigenin Me ether (**II**). Oxidation of (**I**) with $KMnO_4$ does not yield useful products, whereas (**II**) gives *anisole-2 : 3 : 4 : 5-tetracarboxylic acid*, m.p. 250—251°. α-Sorinin appears to be the lactone of *x*-primverosido-1(or 4)hydroxy-*x'*-methoxy-3-hydroxymethyl-2-naphthoic acid. J. N. A.

Constitution of cannabiscitrin. P. S. Rao and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, **14**, **A**, 265—269).—Cannabiscitrin (**I**) is a monoglucoside of the flavanol cannabiscetin with the sugar residue in the 3'-position of the side C_6H_6 nucleus. It resembles butrin. When treated with *p*-$O{:}C_6H_4{:}O$ in abs. EtOH (**I**) gives the gossypetone reaction. Cannabiscitrin acetate is transformed by Me_2SO_4 and NaOH followed by hydrolysis into 3 : 5 : 8 : 4' : 5'-*pentamethylcannabiscitrin*, m.p. 191—192°, further methylated to the Me_6 ether, m.p. 174—175°, and converted by alkaline oxidation into 4 : 5 : 3 : 1-$(OMe)_2C_6H_2(OH)\cdot CO_2H$, m.p. 193—195° (lit. m.p. 184—185°). This is also obtained by first decomp. (**I**) with alkali and then subjecting the products to methylation and subsequent hydrolysis. H. W.

Isolation and constitution of quercetagitrin, a glucoside of quercetagetin. P. S. Rao and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, **14**, **A**, 289—296).—*Quercetagitrin* (**I**) is the 7-glucoside of quercetagetin (**II**). The alcoholic extract of the petals of the African marigold (*Tagetes erecta*) very slowly deposits (**I**), $C_{21}H_{20}O_{13},2H_2O$, m.p. 236—238° (decomp.), and the mother-liquors from (**I**) deposit (**II**), m.p. 314—316° (acetate, m.p. 209—210°), when largely diluted with H_2O. (**I**) is freely sol. in NaOH to a yellow solution and gives a brownish-green colour with $FeCl_3$. In alkaline buffer solutions the most prominent colour of (**I**) is pink, whereby it is readily distinguished from (**II**), which gives a transient green and final brown or brown-red. It yields a brick-red ppt. with $Pb(OAc)_2$ and is hydrolysed with difficulty, showing that it is not a 3-glucoside. Its *nona-acetate* has m.p. 225—227°. Alkaline oxidation and hydrolysis of (**I**) gives veratric acid (**III**), m.p. 183—184°. Methylation ($COMe_2$–Me_2SO_4–20% NaOH) and subsequent hydrolysis (7% H_2SO_4) of (**I**) affords 3 : 5 : 6 : 3' : 4'-*pentamethylquercetagetin* (**IV**), m.p. 234—235°, oxidised in alkaline solution to (**III**). $CH_2{:}CH\cdot CH_2Br$, anhyd. K_2CO_3, and (**IV**) in $COMe_2$ afford 3 : 5 : 6 : 3' : 4'-*pentamethyl-7-allylquercetagetin*, m.p. 122—124° after softening at ~118°, isomerised at 195—200° to 8-*allyl*-3 : 5 : 6 : 3' : 4'-*pentamethylquercetagetin*, m.p. 188—190°, freely sol. in dil. NaOH. H. W.

III.—HOMOCYCLIC.

Manufacture of 1 : 3-dichloro- and 1 : 3 : 5-trichloro-benzenes.—See B., 1941, II, 372.

Factors determining the course and mechanisms of Grignard reactions. IV. Effect of metallic halides on the reaction of aryl Grignard reagents and organic halides. M. S. Kharasch and E. K. Fields (*J. Amer. Chem. Soc.*, 1941, **63**, 2316—2320).—Addition of PhBr (1 mol.) to MgPhBr (1 mol.) + $CoCl_2$ (2·5—7 mol.-%) in Et_2O gives 83—86% of Ph_2 and traces of polyphenyls etc. The Ph_2 is derived from the MgPhBr, since (*a*) the PhBr may be replaced by *p*-C_6H_4MeBr, EtBr, or $Pr^{\beta}Cl$ without greatly affecting the yield, and (*b*) replacing the MgPhBr by *o*- or *p*-$C_6H_4Me\cdot MgBr$, *p*-$OMe\cdot C_6H_4\cdot MgBr$, or *p*-$OEt\cdot C_6H_4\cdot MgBr$ gives 74—95% of the appropriate other diaryl. Yields of Ph_2 obtained by other additions are $NiCl_2$ 72, $FeCl_3$ 47, $MnCl_2$ 21, and CuCl 6%. No reaction occurs between MgArHal and ArHal or between ArHal and the above mentioned metal halides. The reaction, $2MgArX + CoCl_2$ (etc.) → $Ar_2 + 2MgClX + Co$, gives good yields per mol. of $CoCl_2$ etc., but can account for only traces of Ar_2 when only a few mol.-% of $CoCl_2$ etc. are used. The reaction mechanism is: $MgArBr + CoCl_2 \rightarrow CoArCl + MgClBr$; $2CoArCl \rightarrow Ar_2 + 2CoCl$; $CoCl + Ar'Br \rightarrow CoClBr + Ar'\cdot$; $CoClBr + MgArBr \rightarrow$ etc. The polyphenyls are formed from the Ar'· and are thus absent when Ar'Br is replaced by AlkBr. Use of PhCl in place of PhBr gives only 37% of Ph_2, since fission of the Ph–Cl linking is more difficult than that of Ph–Br. Grignard reactions in presence of $CoCl_2$ etc. proceed by the analogous mechanism: $MgRBr + CoCl_2 \rightarrow CoRCl + MgClBr$; $2CoRCl \rightarrow R_2 + 2CoCl$; $2CoCl + 2COPh_2 + MgClBr \rightarrow 2CoCl_2 + (CPh_2\cdot O\cdot MgBr)_2$ etc. Whether reduction or normal addition of MgRBr to $COPh_2$ occurs depends on the relative rates of the normal reaction and of the decomp. of CoRCl. CoPhBr is more stable than CoMeBr; addition of $CoCl_2$ to MgPhBr or MgMeBr in Et_2O and then immediate addition of PhBr causes vigorous reaction, but if the brown-black solution is boiled for 1·5 hr.

there is considerable reaction when PhBr is later added to the aryl (half the yield of Ph_2) but none with the alkyl compound. R. S. C.

Accelerated autoxidation of ethers and unsaturated hydrocarbons in presence of didiphenylene-ethylene. G. Wittig and G. Pieper (*Annalen*, 1941, **546**, 172—179; cf. A., 1939, II, 22).—O_2 has little effect on dioxan (**I**) alone at 25° but in the presence of didiphenylene-ethylene (**II**) the quantity of O_2 absorbed far exceeds that required for the quant. oxidation of (**II**) to fluorenone (**III**). (**I**) appears a suitable substrate in conjunction with (**II**) to initiate oxidative processes in the sense of the mol. adduct, donator···O:O···acceptor. $(CH_2Ph)_2O$ (**IV**) alone absorbs O_2 very slowly but addition of (**II**) causes a great increase in the rate, which returns to its original val. as soon as the oxidation of (**II**) to (**III**) is complete. (**I**) and (**IV**) give peroxides detectable by KI-starch. Treatment with $NaHSO_3$ of (**IV**) which has been oxidised in presence of (**II**) affords appreciable amounts of PhCHO: $CH_2Ph{\cdot}O{\cdot}CHPh{\cdot}O_2H$ (+ $NaHSO_3$) → $CH_2Ph{\cdot}O{\cdot}CHPh{\cdot}OH$ → $CH_2Ph{\cdot}OH$ + PhCHO. Observation of the behaviour of C_6H_6, PhMe, *cyclo*hexene, tetrahydronaphthalene, CCl_4, PhCl, EtOH, Pr$^\beta$OH, Bu$^\gamma$OH, PhOMe, *iso*amyl ether, (**I**), (**IV**), $COMe_2$, COPhMe, EtOAc, Ac_2O, and AcOH towards O_2 in presence of (**II**) shows that only those solvents absorb the gas which can themselves yield peroxides. These are the media in which (**II**) is oxidised to (**III**). The contrast between ethers and alcohols is striking; among the latter only Bu$^\gamma$OH is active and this may be due to the presence in it of $CMe_2{:}CH_2$. The oxidisability of (**II**) depends not on the polarity of the medium but on its ability to yield a peroxide. In the absence of (**II**), the solvents in which (**II**) is oxidised to (**IV**) restrict the autoxidation of PhCHO whereas the solvents in which (**II**) remains unchanged are without action on oxidising PhCHO. The restriction of the oxidation of aldehydes and the oxidisability of (**II**) in various media are due to one and the same cause, viz., the ability of the compounds to form a labile mol. adduct with O_2. In this condition the latter is activated and, in conjunction with the substrate, can initiate oxidations. H. W.

Preparation of diphenylethylene derivatives.—See B., 1941, II, 372.

Polymerisation of styrene in presence of carbon tetrachloride.—See A., 1942, I, 67.

Preparation of diaryldialkylethylene [dialkylstilbene] derivatives.—See B., 1941, II, 372.

Synthesis of αδ-diphenyl-αδ-*p*-tolyl- and αδ-diphenyl-αδ-di-*p*-chlorophenyl-butatriene. D. Simamura (*Bull. Chem. Soc. Japan*, 1941, **16**, 210—213).—Mg acetylenyl bromide and *p*-C_6H_4MeBz or -C_6H_4BzCl give meso- and r-αδ-*diphenyl*-αδ-*di*-p-*tolyl*-, m.p. 156—157° and 151·5°, or -p-*chlorophenyl*-*butinediol*, m.p. 133—134° and 148—148·5°, respectively, converted by P_2I_4–CS_2 into the corresponding $\Delta^{\alpha\beta\gamma}$-*butatrienes*, m.p. 236° (decomp.) and 246—247° (decomp.), respectively (cf. Kuhn *et al.*, A., 1938, II, 226). A. T. P.

Iodination.—See A., 1942, II, 45.

Mobility of groups in chloronitrodiphenyl sulphones. J. D. Loudon and N. Shulman (*J.C.S.*, 1941, 722—727).—2-*Chloro*-6-*nitro*-4′-*methyldiphenyl sulphone*, m.p. 139°, obtained through the *sulphide*, m.p. 69—70°, from 2 : 3 : 4-$C_6H_3Cl_2{\cdot}NO_2$ and $C_6H_4Me{\cdot}SNa$, with $C_5H_{11}N$ and NH_3–MeOH gives respectively the 6-*nitro*-2-*piperidino*-, m.p. 171°, and 2-*chloro*-6-*amino*-compound, m.p. 134—135°. With NaOMe, a mixture containing a small amount of 6 : 2 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}OMe$ and a product forming on reduction ($SnCl_2$–HCl) 2-*amino*-, m.p. 158°, and 2-*chloro*-6-*methoxy*-4′-*methyldiphenyl sulphone*, m.p. 102°, is obtained. 3-Chloro-2-nitro-4′-methyldiphenyl sulphone (**I**) with NaOMe and $C_6H_4Me{\cdot}SH$ affords the 3-*chloro*-2-p-*tolylthio*-compound, m.p. 153—154° [oxidised (H_2O_2) to 2 : 3-*di*-p-*toluenesulphonylchlorobenzene*, m.p. 229°], and 1 : 2 : 6-$NO_2{\cdot}C_6H_3(S{\cdot}C_6H_4Me\text{-}p)_2$, also obtained from 3-*chloro*-2-*nitrodiphenyl sulphone*, m.p. 144°, with NaOH and $C_6H_4Me{\cdot}SH$. 2 : 6-Di-*p*-toluenesulphonylnitrobenzene with NaOH and $C_6H_4Me{\cdot}SH$ yields 2 : 6-*di*-p-*toluenesulphonyl*-4′-*methyldiphenyl sulphide*, m.p. 205°, and with $C_5H_{11}N$, gives the corresponding -*piperidinobenzene*, m.p. 143°. Treatment of (**I**) with $C_5H_{11}N$, MeOH, and NH_3–MeOH affords respectively 2-*nitro*-3-*piperidino*-, m.p. 145°, 3-*chloro*-2-*methoxy*-, m.p. 108—109°, and 3-*chloro*-2-*amino*-4′-*methyldiphenyl sulphone*, m.p. 114°. The general behaviour of various sulphone types is discussed and it is suggested that steric inhibition of resonance is an important factor in reactions of this type. F. R. S.

Methyl derivatives of 3 : 4-benzpyrene. Willgerodt reaction on 3-acylpyrenes. W. E. Bachmann and M. Carmack (*J. Amer. Chem. Soc.*, 1941, **63**, 2494—2499).—α-3-*Pyrenylethyl alcohol* [prep. from 3-acetylpyrene by Al(OPr$^\beta$)$_3$–Pr$^\beta$OH], m.p. 112—112·5°, with PBr_3 gives the bromide, m.p. 108° (decomp.), which by successive condensation with $CH_2(CO_2Et)_2$–Na–C_6H_6, hydrolysis by 40% KOH, and decarboxylation at 180—190° gives β-3-*pyrenyl*-n-*butyric acid*, m.p. 177—178°. Lengthening of the chain {$SOCl_2$–Et_2O–C_5H_5N (drop); CH_2N_2–C_6H_6 [diazoketone, m.p. 116—118° (decomp.)]; Ag_2O–MeOH} then gives γ-3-*pyrenyl*-n-*valeric acid*, m.p. 135·5—136·5°, cyclised by PCl_5 and then $SnCl_4$ in C_6H_6 to 4′-*keto*-1′-*methyl*-1′ : 2′ : 3′ : 4′-*tetrahydro*-3 : 4-*benzpyrene*, m.p. 162—163°. This is reduced by Al(OPr$^\beta$)$_3$–Pr$^\beta$OH to the 4′-*OH*-compound, m.p. 184—185°, which with Pd–C–N_2 at 300—320° gives 1′-*methyl*-3 : 4-*benzpyrene* (50%), m.p. 190—190·8° (vac.) [*picrate*, m.p. 186—186·5°; $C_6H_3(NO_2)_3$ *compound*, m.p. 208·5—209°]. 3-*Pyrenylcarbinol* [prep. from 3-pyrenealdehyde by H_2–PtO_2–EtOH (and a little H_2O) (81%) or Al(OPr$^\beta$)$_3$ (54%)], m.p. 123—124°, and PCl_3–C_6H_6 give the *chloride*, m.p. 144—145°, which with $CH_2(CO_2Et)_2$–Na–C_6H_6 gives Me_2 3-*pyrenylmethylmalonate*, m.p. 112—112·5° (purified by way of the acid). With NaOMe–MeI–MeOH this gives Me_2 3-*pyrenylmethylmethylmalonate* (83%), m.p. 136·5—137·5°, converted by hydrolysis and decarboxylation (190—200°) into β-3-*pyrenylisobutyric acid* (**I**), m.p. 173—174°. By reactions as above this affords the diazo-ketone, m.p. 110—111° (decomp.), γ-3-pyrenyl-β-methyl-n-butyric acid, m.p. 125—135°, 4′-*keto*-2′-*methyl*-1′ : 2′ : 3′ : 4′-*tetrahydro*-3 : 4-*benzpyrene*, m.p. 178—179° (vac.), the crude derived alcohol, m.p. 160—170°, and 2′-methyl-3 : 4-benzpyrene, m.p. 139—140° (corr.; vac.), remelts at 140·0—140·4° (corr.) [$C_6H_3(NO_2)_3$ compound, new m.p. 212·5—213° (corr.)]. Clemmensen reduction of γ-keto-γ-3-pyrenyl-α-methyl-n-butyric acid (*Me* ester, m.p. 105—105·5°) gives 32% of γ-3-pyrenyl-α-methyl-n-butyric acid and thence as above 4′-keto-3′-methyl-1′ : 2′ : 3′ : 4′-tetrahydro-3 : 4-benzpyrene (**II**) (74%), m.p. 178—178·5° (vac.) [lit. 176—177° (corr.)]. 4′-Keto-1′ : 2′ : 3′ : 4′-tetrahydro-3 : 4-benzpyrene, $Me_2C_2O_4$, and NaOMe in C_6H_6 give *Me* 4′-*keto*-1′ : 2′ : 3′ : 4′-*tetrahydro*-3 : 4-*benz*-3-*pyrenylglyoxylate*, m.p. 172—174° (decomp. in Pyrex; lower in soft glass), decomposed at 180—190° to *Me* 4′-*keto*-1′ : 2′ : 3′ : 4′-*tetrahydro*-3 : 4-*benzpyrene*-3′-*carboxylate*, m.p. 154·5—155° (vac.), resolidifies, remelts at 176·5—178·5° (clear at 181°). Condensation thereof with MeI–NaOMe in C_6H_6 and later hydrolysis by boiling HCl–AcOH–H_2O gives (**II**) (33%). Reduction and then dehydration etc. of (**II**) as above gives 3′-methyl-3 : 4-benzpyrene, m.p. 147·5—148° (corr.) after softening (slow heating) [*s*-$C_6H_3(NO_2)_3$ compound, new m.p. 212·5—213°]. Condensation of (**II**) with MgMeI in Et_2O and heating the product with Pd–C at 300—320° gives 3′ : 4′-*dimethyl*-3 : 4-*benzpyrene* (91%), m.p. 215—216° (*picrate*, m.p. 205—205·5°). $(RCO)_2O$, pyrene, and $AlCl_3$ in $PhNO_2$, at successively, −5°, 10°, and 0° give 82—88% of 3-acylpyrenes. With $(NH_4)_2S_x$ in hot dioxan 3-acetylpyrene gives 92% of 3-*pyrenylacetamide*, m.p. 246—247°, hydrolysed to the acid, m.p. 222·5—223° (vac.) [lit. 220° (decomp.)], obtained also in poor yield from 3-chloromethylpyrene by KCN–MeOH, followed by 20% KOH–EtOH. 3-*n*-Propionyl- and 3-n-*butyryl*-*pyrene*, m.p. 73—74°, give similarly β-3-*pyrenylpropionic* (67%), m.p. 178—179° [Me ester, m.p. 95·5—96·5° (corr.) (lit. 81°)], and γ-3-pyrenylbutyric acid (46%), m.p. 186—187° (crude amide, m.p. 172—175°), respectively. 3-iso*Butyryl*-, m.p. 87—89°, and 3-iso-*valeryl*-*pyrene*, m.p. 82—82·5°, do not undergo this reaction. R. S. C.

Thiocyanation of carcinogenic hydrocarbons.—See A., 1942, II, 10.

Nitrons acid as a nitrating and oxidising agent. V. Reactions with the four 3-halogenodimethylanilines. H. H. Hodgson and D. E. Nicholson (*J.C.S.*, 1941, 766—770; cf. A., 1941, II, 319).—*m*-$C_6H_4F{\cdot}NH_2$ and Me_2SO_4–MeOH at 160—170° afford m-*fluoro*-*dimethylaniline* (**I**), b.p. 198—199°/752 mm. (*hydrochloride*, m.p. 153°; *picrate*, m.p. 181°), and (after Ac_2O) -*acetmethylanilide*, m.p. 113°. (**I**) and HCl-aq. $NaNO_2$ (added all at once) yield 3-*fluoro*-4- (**II**), m.p. 120° (2N-NaOH gives the 3-*OH*-compound, m.p. 141—142°), and -2-*nitrodimethylaniline*, b.p. 184°/752 mm., with some 3-*fluoro*-

4-nitrosodimethylaniline (**III**), m.p. 119° (*hydrochloride*) (2N-NaOH gives 4-nitrosoresorcinol). (**I**)–$NaNO_2$–AcOH give (**III**). m-*Fluoroacetanilide*, m.p. 85°, and Ac_2O–fuming H_2SO_4 (27% SO_3)–HNO_3 (*d* 1·5) at 0° yield 3-fluoro-4- and -6-nitroacetanilide, hydrolysed by 50% H_2SO_4–EtOH to 3-*fluoro*-4- (**IV**), m.p. 153° (*Ac* derivative, m.p. 138°), and -6-*nitroaniline* (**V**), m.p. 97° (Ac_2O–AcCl yields the *Ac* derivative, m.p. 85°). (**IV**) is also prepared from *m*-$C_6H_4F{\cdot}NH_2$–PhCHO at 100° (bath), followed by HNO_3 (*d* 1·5)–H_2SO_4 at <5°. (**IV**) or (**V**) and Me_2SO_4–MeOH at 170° afford (**II**) or 3-*fluoro*-6-*nitrodimethylaniline*, m.p. 39°, respectively. *m*-$C_6H_4Cl{\cdot}NMe_2$ (*hydrochloride*, m.p. 170°; *picrate*, m.p. 179°) and HCl–$NaNO_2$ yield 3-*chloro*-2-, m.p. 36°, and -4-*nitrodimethylaniline* (**VI**), m.p. 125—126°, and 4 : 3 : 1-$NO{\cdot}C_6H_3Cl{\cdot}NMe_2$. (**VI**) is obtained by dimethylating the corresponding amine, and 3-*chloro*-6-*nitrodimethylaniline*, m.p. 49°, is prepared similarly. *m*-$C_6H_4Br{\cdot}NMe_2$ (*hydrochloride*, m.p. 194°; picrate, new m.p. 182°) gives 3-*bromo*-2-, m.p. 38°, and -4-*nitrodimethylaniline*, m.p. 128°, with a little 4 : 3 : 1-$NO{\cdot}C_6H_3Br{\cdot}NMe_2$ (2N-NaOH affords 3-bromobenzoquinone-3-oxime), and *m*-$C_6H_4I{\cdot}NMe_2$ (**VII**) (*hydrochloride*, m.p. 165°; *picrate*, m.p. 182°) yields 3-*iodo*-2-, m.p. 50°, and -4-*nitrodimethylaniline*, m.p. 140°, and small amounts of 4 : 3 : 1-$NO{\cdot}C_6H_3I{\cdot}NMe_2$ (yields 3-iodobenzoquinone-4-oxime) and -$NO_2{\cdot}C_6H_3I{\cdot}NMe_2$. (**VII**) and excess of HNO_3 (*d* 1·42) give the corresponding *nitrate*, reddens at 120°, decomp. at 202°. A. T. P.

Chemotherapy of bacterial infections. III. *N'-β*-**Phenylethylsulphanilamides.** P. L. N. Rao (*J. Indian Chem. Soc.*, 1941, **18**, 316—320; cf. A., 1940, II, 274).—*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ and $Ph{\cdot}[CH_2]_2{\cdot}NH_2$ in aq. NaOH yield, after hydrolysis of the resulting *Ac* compound, m.p. 126°, by 10% aq. HCl, N'-*β*-*phenylethylsulphanilamide*, m.p. 143° (*hydrochloride*, m.p. 225°). Similarly prepared are: N'-*β*-p-*methoxy*- (**I**), m.p. 149° [*Ac* derivative, m.p. 157°; *hydrochloride*, m.p. 218—219° (decomp.)], -3 : 4-*dimethoxy*-, m.p. 126—127°, and -p-*nitrophenylethylsulphanilamide*, m.p. 207° [*Ac* derivative, m.p. 183—184°; *hydrochloride*, m.p. 202° (decomp.)], and thence (Sn–aq. HCl) the p-NH_2-compound, m.p. 154—155° (*diacetate*, m.p. 230°); dl-N'-ac-*tetrahydro-β-naphthylsulphanilamide*, m.p. 163° [*Ac* derivative, m.p. 190—191°, is hydrolysed by aq. NaOH; *hydrochloride*, m.p. 204—206° (decomp.)]. (**I**) and conc. HBr (reflux) give a product, (?) $C_{14}H_{16}O_3N_2S$, m.p. ~185° (decomp.). *p*-$NH_2{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}NHBz$ yields N'-4-*β*-*benzamidoethylphenylacetylsulphanilamide*, m.p. 198—200°, hydrolysed by aq. NaOH to N'-4-*β*-*aminoethylphenylsulphanilamide*, m.p. 243° (*Ac* derivative, m.p. 223°; *dihydrochloride*, decomp. 210°). A. T. P.

Dinitro-*o*-toluidines. A. McGookin (*J.S.C.I.*, 1941, **60**, 297).—Improved yields are obtained as follows: 3 : 5-dinitro-*o*-tolyl Me ether (prep. described) with MeOH–NH_3 gives 3 : 5-dinitro-*o*-toluidine (99% yield). Nitration of 6-nitroacet-*o*-toluidide affords 93% of mixed toluidides which yield 76% of the 3 : 6- and 14% of the 5 : 6-compound on hydrolysis and fractional crystallisation. W. C. J. R.

2-Chloro-4'-aminodiphenyl.—See B., 1941, II, 415.

***s*-Di*cyclo*hexylethylenediamines.**—See B., 1941, **II**, 415, 446.

Substituted 4 : 4'-diaminodiphenyl sulphones.—See B., 1941, III, 343.

***p*-Aminobenzenesulphonylcarbamides.**—See B., 1941, III, 343.

Associating effect of the hydrogen bond.—See A., 1942, II, 63.

Amidine sulphanilamides.—See B., 1941, III, 344.

Quantum-mechanical calculations applied to the theory of organic dyes. II.—See A., 1942, I, 45.

Cleavage of arylazo-β-naphthylamines by alcoholic hydrochloric acid. H. H. Hodgson and C. K. Foster (*J.C.S.*, 1941, 755—757).—Benzene-, 2- or 4-methoxybenzene- (**I**), 4-hydroxybenzene-, and 4-chlorobenzene-azo-*β*-naphthylamine (slow reaction) are decomposed by refluxing with HCl (*d* 1·16)–EtOH, giving (in all cases) *β*-$C_{10}H_7{\cdot}NH_2$ (**II**) and a diazonium compound, which in presence of the EtOH affords also PhOEt, PhOMe, PhOH + *pp'*-azophenol, and PhCl, respectively. *o*- or *p*-Toluene- and *α*- or *β*-naphthalene-azo-*β*-naphthylamine with HCl–MeOH similarly afford (**II**) and *o*- or *p*-$C_6H_4Me{\cdot}OMe$ and *α*- or *β*-$C_{10}H_7{\cdot}OMe$, respectively. 2-Chloro-, 2 : 5-dichloro-, and *o*-, m-, or *p*-nitro-benzeneazo-*β*-naphthylamine do not decompose similarly (24 hr.). (**I**) and HCl–EtOH–CuCl give (**I**) + *p*-$C_6H_4Cl{\cdot}OMe$, whereas (**I**) and HCl–EtOH (after 1 hr.) yield *p*-$OMe{\cdot}C_6H_4{\cdot}N_2X$ and thence *p*-$OMe{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$-*β*. Mechanism of reaction is discussed. A. T. P.

Arylazodiguanides.—See B., 1941, II, 416.

Diazotisation. J. C. Earl and N. G. Hills (*Chem. and Ind.*, 1941, 834—835).—The fundamental reaction of primary or *sec.* amines with HNO_2 is formation of NRR'·N(OH)$_2$. The rather analogous views of Kenner (A., 1941, II, 220) are criticised. R. S. C.

Interpretation of the Sandmeyer reaction. H. H. Hodgson, S. Birtwell, and J. Walker (*J.C.S.*, 1941, 770—776).—Cu^I halides react with diazonium salts mainly by two mechanisms, viz., (*a*) formation of a complex anion, *e.g.*, $[Cu_2Cl_2Br_2]^{--}$, with HX; attack by the anionoid halogen of this complex at the cationoid aryl C atom to which the N_2 group is linked; release of an electron from the halogen to the N through the C; and final covalent linking of halogen to the C; and (*b*) oxidation of the Cu_2X_2 to CuX_2 by cationoid N_2 ion, involving release of an election by the Cu to the N, with linkage of aryl radicals to give diaryls. The action of HI on ArN_2X is explained by mechanism (*a*). PhN_2Cl added to Cu_2Cl_2 (in much H_2O) affords PhCl, but when the sequence of addition is reversed, much Ph_2 and *p*-$C_6H_4Ph{\cdot}OH$ are also formed (oxidation by diazonium salt when in excess). The effect of substituents in the nucleus on diaryl formation is examined, and a method for determining amounts of $CuCl_2$ formed in the Sandmeyer reaction (in CO_2) is described. The mechanism of the catalytic action of Cu^{II} salts on diazonium compounds is similar to that for Cu^I salts. The anomalous behaviour of HF is discussed. ArN_2Cl (Ar = 2-, 3-, and 4-$C_6H_4{\cdot}NO_2$; 4-$C_6H_4{\cdot}NH_2$; 4-C_6H_4Cl and -C_6H_4Br; C_6H_4Ph), diazotised in AcOH–$NaNO_2$–H_2SO_4 at <20°, treated with Cu_2Cl_2–HBr or (Ar = 2-$C_6H_4{\cdot}CO_2H$ also) Cu_2Br_2–HCl, respectively, afford yields of the resulting Br- to Cl-compounds of ~90—96 : 4—10%, or ~30—35 : 65—70%, respectively; in the former case, the halogen comes mainly from the HBr. *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ (**I**), diazotised in HCl at 0°, an equiv. of HBr added, followed by excess of Cu powder, or (**I**) diazotised in conc. H_2SO_4, with aq. NaCl–NaBr–Cu, affords 85% of *p*-$C_6H_4Br{\cdot}NO_2$ (**II**) [+ *p*-$C_6H_4Cl{\cdot}NO_2$ (**III**) and *p*-$NO_2{\cdot}C_6H_4{\cdot}OH$], whilst (**I**)–AcOH–$NaNO_2$–$H_2SO_4$ and Cu_2Br_2 or Cu_2Cl_2 in HCl–HBr give 96 or 94% of (**II**) and 4 or 6% of (**III**), respectively (overwhelming replacement by Br). (**I**)–AcOH–$NaNO_2$–H_2SO_4 and Cu_2I_2–HCl or –HBr afford *p*-$C_6H_4I{\cdot}NO_2$ in 80 or 75% yield, with (**III**) or (**II**), respectively. *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ in HCl with $NaHSO_3$ gives *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2{\cdot}HCl$, but when the HCl is replaced by AcOH, $NaHSO_3$, or $Na_2S_2O_4$, with or without KI, little action occurs, but addition of $CuSO_4$ affords *p*-$C_6H_4I{\cdot}NO_2$. With *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ and Cu_2Br_2–HCl, a decrease in concn. of Cu_2Br_2 shows an increase in replacement by Cl, although not proportionately. A mechanism of the formation of naphthalene 1 : 8-sultone from 8 : 1-$SO_3H{\cdot}C_{10}H_6{\cdot}N_2X$ is suggested. A. T. P.

Oxidation of 4-octyl*cyclo*hexanol.—See B., 1941, II, 417.

Physicochemical properties and mechanism of electrochemical reduction of the chromophoric nitrosobenzene group.—See A., 1942, I, 39.

Tri*cyclo*hexyl phosphites.—See B., 1941, II, 417.

Aryl phosphates.—See B., 1941, II, 417.

Stilbœstryl hydrogen phosphates and sulphates.—See B., 1941, II, 417.

***cyclo*Hexylamine salts of nitrophenols.**—See B., 1941, II, 417.

Alkylation of phenols.—See B., 1941, II, 416.

Aromatic substitution. IV. Action of fuming nitric acid on 3-fluoroanisole and 3-fluoro-2-, -4-, and -6-nitroanisole. H. H. Hodgson and J. Nixon (*J.C.S.*, 1941, 793; cf. A., 1930, 1281).—m-$C_6H_4F{\cdot}OMe$ or 4 : 3 : 1-$NO_2{\cdot}C_6H_3F{\cdot}OMe$ and HNO_3 (*d* 1·5) at 0° or 50° yield 3-*fluoro*-4 : 6-*dinitroanisole*, m.p. 99°. 2 : 3 : 1- and 6 : 3 : 1-$NO_2{\cdot}C_6H_4F{\cdot}OMe$ similarly yield 3-*fluoro*-2 : 6-*dinitroanisole*, m.p. 90°, at 0°, but give 3 : 2 : 4 : 6 : 1-$C_6HF(NO_2)_3{\cdot}OMe$ at 50°. Replacement of all 3 Cl by NO_2 when 2 : 4 : 6 : 3 : 1-$C_6HCl_3F{\cdot}OMe$ is treated with HNO_3 (*d* 1·5) at 0° thus appears to be in the sequence 6-, 2-, and 4-. A. T. P.

Naphthalene derivatives.—See B., 1941, II, 415; **III**, 344.

Benzoylbenzoic acid derivatives.—See B., 1941, II, 418.

Sodium antimonylpyrocatechol thiosalicylate.—See B., 1941, III, 344.

*N-cyclo*Hexyl-*NN*-dimethylammonium *N-cyclo*hexyl-*N*-methyldithiocarbamate.—See B., 1941, II, 445.

***cyclo*Pentane series. I. Synthesis of 1-methyl*cyclo*pentane-1 : 2-dicarboxylic acid in *cis*- and *trans*-forms.** P. C. Dutta (*J. Indian Chem. Soc.*, 1940, **17**, 611—618).—Et methyl*cyclo*pentanonecarboxylate and HCN give *Et* 2-*cyano*-2-*hydroxy*-1-*methyl*cyclo*pentanecarboxylate*, b.p. 122°/4 mm., which with $SOCl_2$–C_5H_5N affords *Et* 2-*cyano*-1-*methyl*-Δ^2-cyclo*pentenecarboxylate*, b.p. 100—102°/4 mm., hydrolysed to 1-*methyl*-Δ^2-cyclo*pentene*-1 : 2-*dicarboxylic acid*, m.p. 204°. Reduction (Na–Hg) of this acid leads to trans-1-*methyl*cyclo*pentane*-1 : 2-*dicarboxylic acid* (**I**), m.p. 142°. *Me* γ-*ethoxypropyl ketone*, b.p. 169°, obtained by hydrolysis (H_2SO_4) of *Et* γ-*ethoxy*-α-*acetobutyrate*, b.p. 110—113°/7 mm., with HCN followed by CN·CH_2·CO_2Et, yields *Et* αβ-*dicyano*-β-(γ-*ethoxypropyl*)*butyrate*, b.p. 170—175°/7 mm., also obtained from KCN and *Et* α-*cyano*-β-(γ-*ethoxypropyl*)*crotonate*, b.p. 135°/5 mm. (from the ketone with CN·CH_2·CO_2Et and NH_4Ac). The $(CN)_2$-ester cannot be cyclised successfully and hydrolysis with H_2SO_4 gives *Et* α-*methyl*-α-(γ-*ethoxypropyl*)*succinate*, b.p. 134°/5 mm. *Et* αδ-*dibromovalerate*, b.p. 111—112°/5 mm., obtained from Et γ-bromopropylmalonate by treatment with $SOCl_2$ followed by Br, with CN·CH_2·CO_2Et–Na affords Et_2 1-cyano*cyclo*pentane-1 : 2-dicarboxylate, hydrolysed to the crude acid, from which the cis-*form*, m.p. 141°, of (**I**) can be isolated through the anhydride. *Et* δ-*bromo*-α-*carbethoxy*-α-*methylvalerate*, b.p. 153—155°/12 mm., obtained from $CMeNa(CO_2Et)_2$ and $(CH_2)_3Br_2$, after hydrolysis and treatment with PBr_5, affords *Et* αδ-*dibromo*-α-*methylvalerate*, b.p. 118—120°/6·5 mm., which with CN·CH_2·CO_2Et–Na gives *Et*$_2$ 1-*cyano*-2-*methyl*cyclo*pentane*-1 : 2-*dicarboxylate*, b.p. 118—120°/1 mm. This ester is hydrolysed to (**I**). The methods of interconversion of the *cis*- and *trans*-forms are described.

F. R. S.

Synthesis of hexahydro*iso*phthalic acid. P. C. Dutta (*J. Indian Chem. Soc.*, 1940, **17**, 607—610).—Na–EtOH, $Et_2C_2O_4$, and 2-cyano-3-methyl*cyclo*hexene give *Et* (3-*cyano*-4-*methyl*-Δ^2-cyclo*hexenoyl*)*formate*, m.p. 110°, which distils unchanged at 170°/9 mm. Similarly 2-cyano*cyclo*hexene affords *Et* (3-*cyano*-Δ^2-cyclo*hexenoyl*)*formate*, m.p. 106°, b.p. 156°/5 mm.; the corresponding *acid*, m.p. 197—199° (decomp.), was submitted to oxidation (H_2O_2) at 60°, then reduced (Na–Hg), after which esterification gave *Et hexahydro*iso*phthalate*, b.p. 124°/5 mm. Hydrolysis (HCl) of the ester gives the *cis*- and the *trans*-acids, from which the former was isolated through the anhydride.

F. R. S.

Addition of maleic anhydride and ethyl maleate to substituted styrenes. B. J. F. Hudson and (Sir) R. Robinson (*J.C.S.*, 1941, 715—722).—*iso*Safrole (**I**) and maleic anhydride (**II**) in xylene (reflux) give a polymeride, m.p. >260° (decomp.), and the adduct, 6 : 7-*methylenedioxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1 : 2-*dicarboxylic anhydride* (**III**), m.p. 142—143° [*phenylimide*, m.p. 243°; the corresponding acid is readily converted by heat into (**III**)]. (**III**) and Pd–C (S gives a S-containing product, m.p. 237°) at 300° (CO_2) afford 6 : 7-*methylenedioxy*-3-*methylnaphthalene*-1 : 2-*dicarboxylic anhydride*, m.p. 242—243°, also obtained from piperonylallylene and (**II**) in xylene at 150°. (**I**) and Et_2 maleate (**IV**) give the Et_2 ester *adduct*, m.p. 92—93°, b.p. 205—210°/1·3 mm., which is hydrolysed by KOH–EtOH to the dicarboxylic acid and thence affords (**III**). (**I**) and (:C·CO_2Et)$_2$ at 100° (bath), then at 200° (5 min.), yield 6 : 7-*methylenedioxy*-3-*methyl*-3 : 4-*dihydronaphthalene*-1 : 2-*dicarboxylic anhydride*, m.p. 178°. *iso*Eugenol refluxed with (**IV**) gives an *adduct*, b.p. 236—237°/1·5 mm., and thence (BzCl) *Et*$_2$ 7-*benzoyloxy*-6-*methoxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1 : 2-*dicarboxylate*, m.p. 117—118°. *O*-Methyl*iso*eugenol (**V**) and (**I**) in xylene afford 6 : 7-*dimethoxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1 : 2-*dicarboxylic anhydride*, m.p. 107° (*phenylimide*, m.p. 163°), oxidised ($KMnO_4$) to metahemipinic acid. (**V**) and (**IV**) give the Et_2 ester *adduct*, m.p. 70°, b.p. 212—214°/1·5 mm. (reaction is reversible), dehydrogenated (Pd–C) to 6 : 7-*dimethoxy*-3-*methylnaphthalene*-1 : 2-*dicarboxylic anhydride*, m.p. 250—251° ($C_2H_4Cl_2$) or 251—252° (AcOH). *trans-O*-Ethyl*iso*eugenol and (**I**) give heteropolymerides only, but the *cis*-isomeride yields 6-*methoxy*-7-*ethoxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1 : 2-*dicarboxylic anhydride*, m.p. 130—131°, and the *dicarboxylic acid*, m.p. 208—209° (decomp.), is obtained by hydrolysis of the Et_2 ester *adduct*, m.p. 105—106°, prepared from (**IV**). 2 : 3 : 1-Dimethoxypropenylbenzene and (**I**) give a heteropolymeride, m.p. 180—200°, and 5 : 6-*dimethoxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1 : 2-*dicarboxylic anhydride*, m.p. 159—160°. Piperonal and MgBuBr give a product [containing (probably) *piperonylbutylcarbinyl ether*, b.p. 206—208°/1 mm., piperonylcarbinol, piperonylbutylcarbinol, and piperonylpentene], distilled to give α-*piperonyl*-Δ^α-*pentene*, b.p. 273—276°, which with (**I**) affords an adduct, 6 : 7-*methylenedioxy*-3-*propyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1 : 2-*dicarboxylic anhydride*, m.p. 138°. No adduct is obtained from (**I**) and CH_2:CH·CHO, *p*-O:C_6H_4:O, or 1 : 4-O:$C_{10}H_6$:O, from (**I**) and piperonyl acrylate, β-bromopiperonylethylene, piperonylacetylene, b.p. 90°/3 mm., or *m*-hydroxystyrene (**VI**), b.p. 119—120°/16 mm., from (**I**) or (**II**) and *m*-methoxystyrene, b.p. 90°/5 mm., or *m*-methoxypropenylbenzene, b.p. 128—129°/20 mm., or from *cyclo*pentadiene (**VII**) and *o*-$C_6H_4(CO)_2O$. *m*-OBz·C_6H_4·CHO (*semicarbazone*, m.p. 209°) and MgMeI give a product, hydrolysed by aq. KOH–EtOH to (**VI**). 2 : 3-$(OMe)_2C_6H_3$·CHMe·OH is dehydrated on distilling with steam to give (impure) 2 : 3-dimethoxystyrene. *p*-Methoxystyrene and (**I**) at 100° (bath) yield a *heteropolymeride*. 2 : 3-Methylenedioxystyrene and (**I**) in C_6H_6 or PhMe at 0° give a *polymeride*, (?) $C_{26}H_{20}O_{10}$, m.p. ~250° (constitution not determined). Anethole and (**I**) in xylene give a *polymeride*, (?) $C_{60}H_{58}O_{10}$, m.p. 153—154°. Me benzylidenepyruvate, m.p. 74—75°, and (**VII**) in MeOH afford an adduct, hydrogenated (Pd–C at 2—3 atm. in MeOH) and then hydrolysed to an oil [*semicarbazone*, m.p. 207—208° (decomp.)]. 2 : 3 : 1-(OMe)$_2$C$_6$H$_3$·CHO, $AcCO_2H$, and aq. NaOH at 20—30° give *Me* 2 : 3-*dimethoxybenzylidenepyruvate*, m.p. 63°, b.p. 188—189°/0·4 mm., which with (**VII**) in EtOH at room temp. gives *Me* 5-2′ : 3′-*dimethoxyphenyl*-3 : 6-*methylene*-Δ^1-cyclo*hexene*-4-*oxalate*, m.p. 74—75°. OAlk *p*- to the unsaturated side-chain of a styrene enhances the tendency to unite with (**II**), whereas *m*-OAlk appears to exert a stabilising influence. When *p*- and *m*-OAlk are present, reaction is less facile than with the simple *p*-substituted compounds; $C_{10}H_8$ derivatives (1 : 1 adducts) are only obtained when there is a *m*-OAlk *p*- to the C of the C_6H_6 ring involved in the cyclisation and when the styrene derivative is β-alkylated. Theoretical aspects are discussed.

A. T. P.

Synthesis of phenanthrene derivatives. P. C. Guha and S. Krishnamurthy (*J. Indian Inst. Sci.*, **23**, **A**, 183—190).—*cyclo*Hexanone does not condense with $C_2H_4Br_2$ in presence of $NaNH_2$–PhMe. Et *cyclo*hexanone-2-carboxylate with $C_2H_4Br_2$ gives *Et*$_2$ 2 : 2′-*diketo*-αβ-*dicyclohexylethane*-1 : 1′-*dicarboxylate*, b.p. 127—129°/10 mm. (*pyrazalone* derivative, m.p. 296°), also obtained from the ester with C_2H_4–K–xylene, and hydrolysed either by acid or alkali to the corresponding *acid*, m.p. 102—103°. The ester does not undergo pinacone reduction with either Al–$HgCl_2$ or Na–Hg.

F. R. S.

Restricted and accelerated autoxidation of benzaldehyde in presence of didiphenylene-ethylene. G. Wittig and G. Pieper (*Annalen*, 1941, **546**, 142—171; cf. A., 1940, II, 45).—The absorption of O_2 by PhCHO (**I**) alone and dissolved in CCl_4 and PhCl has been measured at 25°/760 mm., and simultaneously the concns. of BzO_2H (**II**) and BzOH (**III**) have been determined iodometrically and acidimetrically respectively. Within the actual time the rate of absorption is const. since the conditions are const. and so little PhCHO is oxidised that its concn. is not greatly affected. The peroxidic O curves all show a more or less pronounced max. and then tend towards a const. val. Since in CCl_4 these graphs coincide with those of total oxidation it appears that almost the total O is at first in peroxidic union and that the production of (**III**) is a secondary reaction: (**I**) + O_2 → (**II**) and (**II**) + (**I**) = 2(**III**). The subsequent diminution of the concn. of (**II**) is due to the acceleration of the second change by (**III**). Pre-addition of (**III**) diminishes the concn. of (**II**) and removes the max. The action of (**II**) on a large excess of (**I**) is a change of the first order and proceeds about twice as rapidly in PhCl as in CCl_4. Constancy of k is attained only after 5 min. and the primary, very rapid action is attributed to an unstable additive product: (**I**) + (**II**) → BzO_2·CHPh·OH or OH·CPh$<^{O_2}_{O\cdot}>$CHPh (**IV**) → 2(**III**). The rapid formation of (**IV**) leads to an equilibrium so that 10—20% of the (**II**) is not detected iodometrically. The simultaneous increase in

the concn. of (III) is due to the instability of (IV) to dil. alkali. The subsequent normal decline in the concn. of (II) is attributed to the decomp. of (IV) into 2 mols. of (III) which occurs slowly and therefore controls the rate of the reaction. Comparison of the rate of decline of the concn. of (II) during the autoxidation of (I) and the action of (II) on (I) shows agreement between the observed and calc. vals. of (II) until (II) has attained its max. and thereafter a divergence which is more pronounced in PhCl. This is due in part to the accelerating acton of the (III) produced and this is ascribed to an accelerated production of (IV). In CCl_4 (III) is produced so slowly that it does not immediately affect the production of (IV) to any considerable extent whereas in PhCl it is much more rapidly produced. It is considered improbable that the catalytic action of (III) can entirely account for the divergences between the observed and calc. vals. in PhCl and in pure (I), and the formation of a mol. adduct of (I) and O_2 is postulated: (I) + O_2 → PhCHO··O:O·· (V) → (II) or (V) → CHPhO···O:O···CHPhO → [$PhCHO_2$ + O_2CHPh] → 2(III). The existence of an active form of (II) explains the oxidation of ωω′-tetraphenylpolyenes by autoxidising (I) although they are stable to O_2 and to "synthetic" (II) even in presence of (I). Simultaneously the oxidation of (I) is markedly repressed. Addition of small quantities of didiphenyleneethylene (VI) to autoxidising (I) without solvent or in presence of CCl_4 or PhCl considerably diminishes the rate of absorption of O_2, which becomes nearly normal after (VI) has been oxidised to fluorenone (VII). Oxidation of (VI) and its inhibiting action are closely related but (VI) in CCl_4 or PhCl alone is stable to O_2 even in sunlight. In presence of (VI) the concn. of (II) is greatly diminished and that of (III) in relation to (II) is increased. (VI) has no influence on the oxidation of (I) by (II) in CCl_4 and little effect in PhCl and is not oxidised by (II). Hence the restriction of the autoxidation of (I) must be ascribed to delay in the formation of (II). A scheme is suggested to explain this delay. If the concn. of (VI) is largely increased an acceleration of the oxidation is observed. After a considerable period the inhibiting action of (VI) is apparent and this is followed by a normal rate of oxidation as soon as the conversion of (VI) into (VII) is complete. So long as (VI) is present the concn. of (II) is reduced almost to zero and when (VI) has been oxidised the concn. increases considerably and tends towards the max. observed in the autoxidation of pure (I). For a long period the graph for the formation of (III) is coincident with that of the oxidation of (I). It therefore appears probable that (VI) combines with 1 mol. of O_2 and gives with (I) the same mol. adduct which results from the action of (V) with (VI). In both cases the aggregate passes into (I) + (VII). Since (VI) alone is indifferent to O_2 in CCl_4, the oxidation of the unsaturated hydrocarbon can only occur when the mol. adduct from O_2 and (VI) finds a substrate which can itself enter into mol. union with O_2; in this case the bridging O is distributed uniformly over the two components; with small concns. of (VI) retardation of absorption of O_2 predominates since the formation of this adduct breaks a whole chain of oxidisable mols. of (I). This effect is still more pronounced with increased concn. of (VI) but the accelerated oxidation of (I) by (VI) becomes more obvious. Since the action of 1 : 8-diphenylacenaphthylene on autoxidising (I) gives the cyclic acetal and not the expected Bz_2 compound, the scheme outlined for (VI) cannot be applied to all unsaturated hydrocarbons. The delaying action towards autoxidising (I) is common to all but the chemical changes differ from case to case. H. W.

Catalytic action of Japanese acid earth. XI. Isomerisation of aldehydes to ketones and explanation of the migration of the radicals from the electronic viewpoint. K. Ishimuri (*Bull. Chem. Soc. Japan*, 1941, **16**, 196—209; cf. A., 1935, 455).—The aldehyde is passed over Japanese acid earth at 300° (in CO_2), and in some cases then at 350—450° under reduced pressure, and the ketones produced are examined. CHArAr′·CHO (I) (Ar = Ph; Ar′ = *p*-C_6H_4Me) affords *p*-$C_6H_4Me{\cdot}CH_2{\cdot}COPh$ only, *i.e.*, only Ph migrates; (I) (Ar and Ar′ = *m*- and *p*-C_6H_4Me) gives only *p*-$C_6H_4Me{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4Me$-*m*. (I) (Ar and Ar′ = *o*- and *p*-C_6H_4Me) affords a mixture of *p*-$C_6H_4Me{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4Me$-*o* and *o*-$C_6H_4Me{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4Me$-*p* (4 : 1), and (I) (Ar = *p*-C_6H_4Me; Ar′ = *p*-C_6H_4Cl) yields *p*-$C_6H_4Me{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4Cl$-*p* and *p*-$C_6H_4Cl{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4Me$-*p* (10 : 1). Thus the order of migratory tendency is Ph > *m*-C_6H_4Me > *p*-C_6H_4Cl > *o*-C_6H_4Me > *p*-C_6H_4Me. Mechanisms of isomerisation and results are discussed on the electronic theory basis. Aldehydes are prepared according to the scheme: $COAr{\cdot}CH_2Br$ → $COAr{\cdot}CH_2{\cdot}OAc$ → $COAr{\cdot}CH_2{\cdot}OH$ → $OH{\cdot}CArAr'{\cdot}CH_2{\cdot}OH$, converted by $H_2C_2O_4$ at 115° or aq. H_2SO_4 at 180° into (I). Ketones are identified by Beckmann rearrangement of their oximes or by synthesis from $CH_2Ar{\cdot}COCl$–Ar′H–$AlCl_3$ to give $CH_2Ar{\cdot}COAr'$, also obtained from $CH_2Ar{\cdot}CN$ and MgAr′Br, or from $CH_2Ar{\cdot}CHO$–MgAr′I, followed by oxidation of the diarylcarbinol. When *m*-tolyl-*p*-tolylacetaldehyde is purified through its $NaHSO_3$ additive compound or when it is oxidised to the corresponding acid with moist Ag_2O, much *m*-$C_6H_4Me{\cdot}CO{\cdot}C_6H_4Me$-*p* is formed. Isomeric xylyl compounds can be purified at the $C_6H_3Me_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ stage. $CH_2Ar{\cdot}COAr'$ are converted in air or light (several months) into mixtures of the corresponding arylacetic acids. A. T. P.

Electrolytic reduction of benzophenone in acidic and in alkaline media. S. Swann, jun., S. W. Briggs, V. C. Nekfutin, and A. J. Jerome (*Trans. Electrochem. Soc.*, 1941, **80**, *Preprint* 26, 323—333; cf. A., 1932, 705).—The best cathodes for the electrolytic reduction of $COPh_2$ to benzpinacol in H_2SO_4–EtOH solution are Hg and Al. The latter gives highest yields when etched and coated with a uniform anodic film. Cu and Bi cathodes give small yields but Cd, Sn, Pb, Zn, Ni, and Fe are inactive. Reduction of $COPh_2$ in aq. Na and K xylenesulphonate solution or in aq.-EtOH solutions of KOAc gives good yields of $CHPh_2{\cdot}OH$, especially at Hg and Cd cathodes, and only Ni, Co, Fe, and Mg electrodes are found to be unfavourable to the reduction. In KOAc solution, a limiting c.d. is reached at 0·02 amp. per sq. cm., and in some cases the yields at 80—85° are > at 60°. 30% KOAc yields more consistent results than 10% KOAc. J. W. S.

***iso*Benzoxazoles. IV.**—See A., 1942, II, 66.

***iso*Benzoxazoles [benz*iso*oxazoles]. V. Acetylation of *p*-, *o*-, and *m*-bromotoluene by the Friedel-Crafts method.** W. Borsche and A. Herbert (*Annalen*, 1941, **546**, 277—292).—Repetition of the work of Claus (A., 1892, 1200) on the acetylation of *p*-C_6H_4MeBr in presence of $AlCl_3$ with AcCl as diluent shows that the bromoacetamidotoluene, m.p. 164°, obtained by Beckmann transformation of the bromoacetotoluene-oxime, m.p. 109°, is the 2 : 4- and not the 3 : 4-derivative. Treatment of the crude ketone with 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ leads to the isolation of the 2 : 4-dinitrophenylhydrazones of 2 : 5 : 1- (I), m.p. 194°, and 3 : 6 : 1-$C_6H_3MeBr{\cdot}COMe$ (II), m.p. 170°, and 4-*bromo*-3-*methylacetophenone* (III), m.p. 235°. The first runnings consist essentially of unchanged *p*-C_6H_4MeBr but contain also *p*-$C_6H_4Me{\cdot}COMe$ (IV), detected as the 2 : 4-dinitrophenylhydrazone, m.p. 246°. The structure of all the dinitrophenylhydrazones has been established by comparison with controls obtained from pure ketones. Independently the constitution of (I) is established by the properties of its oxime, m.p. 109°, and by its oxidation ($KMnO_4$) to 2 : 5 : 1-$C_6H_3MeBr{\cdot}CO_2H$ or (II), by production of 2 : 4-dimethyl*iso*benzoxazole by heating the crude oxime with alkali hydroxide, and of (III) by the isolation of 3 : 4 : 1-$C_6H_3MeBr{\cdot}CO_2H$ among the products of oxidative degradation. The mixture consists mainly of (I) and (III) with only a small quantity of (II). Similar treatment of the crude product of the action of AcCl on *p*-C_6H_4MeBr in presence of $AlCl_3$ and CS_2 (Mayer *et al.*, A., 1922, i, 865) shows the presence of (I), (II), (III), and 2 : 4 : 1-$C_6H_3MeBr{\cdot}COMe$ (V) but the presence of 4 : 2 : 1-$C_6H_3MeBr{\cdot}COMe$ (2 : 4-*dinitrophenylhydrazone*, m.p. 161°) could not be detected; the "cryst. oxime," m.p. 112—114°, is not homogeneous. The production of (IV) is not regarded as due to the direct replacement of Br by Ac but to direct acetylation of PhMe formed by disproportionation: $2C_6H_4MeBr = PhMe + C_6H_3MeBr_2$. (III) and (V) probably arise similarly from *o*- and *m*-C_6H_4MeBr obtained by wandering of Br under the influence of $AlCl_3$. The possibility that (III) and (V) are produced from (II) and (I) is experimentally excluded. Re-examination of Claus' data on the acetylation of *o*- (VI) and *p*- (VII) -C_6H_4MeBr gives no reason to doubt the homogeneity of the products. 3 : 4 : 1-$C_6H_3MeBr{\cdot}COMe$, b.p. 156—160°/20 mm., m.p. 31—32° (2 : 4-*dinitrophenylhydrazone*, m.p. 234—235°; *oxime*, m.p. 108°), obtained from (VI) is identical with that derived from 2-*bromo*-5-*cyanotoluene*, m.p. 55°, obtained from 1 : 2 : 5-$C_6H_2MeBr{\cdot}NH_2$. Similarly the ketone from (VII), b.p. 131—133°/17 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 164°; *oxime*, m.p. 102°), is identical with that from 1 : 3 : 6-$C_6H_3MeBr{\cdot}CN$.

The following appear to be new : *4-bromo-2-cyanotoluene*, m.p. 50°; *5-bromo-2-methylacetophenoncoxime*, m.p. 113—114°; 2 : 5-*dimethylbenz*isooxazole, b.p. 122—124°/14 mm. (*4-nitro*, m.p. 161°, and *6-nitro*, m.p. 106—110°, derivatives). H. W.

Isomeric transformations of α-keto-alcohols. III. Benzoylethyl- and propionylphenyl-carbinol. T. I. Temnikova and E. F. Afanasieva. **IV. Reaction of benzoylethyl- and propionylphenyl-carbinol with magnesium organic compounds and with acid chlorides.** T. I. Temnikova (*J. Gen. Chem. Russ.*, 1941, **11**, 70—76, 77—91).—III. COPh·CHEt·OAc is hydrolysed to *α-benzoylpropanol* (**I**), b.p. 131·5—132·5°/12 mm. (*phenylurethane*, m.p. 162—163°). This yields an equilibrium mixture of (**I**) 60—65% and COEt·CHPh·OH (**II**) 35—40% when dissolved in 2% KOH in EtOH; a mixture of the same composition is obtained similarly from (**II**).

IV. (**I**) with MgRBr yields glycols of the general formula OH·CPhR·CHEt·OH [R = *Me*, b.p. 148—149·5°/11·5 mm., *Et* (**III**), m.p. 67—68°, *Pr*$^{\alpha}$, m.p. 78·5—79°]. With (**II**) the products are OH·CHPh·CEtR·OH {R = Me, Et [(**III**) obtained as a by-product], *Pr*$^{\alpha}$}. With MgPhBr, (**I**) yields a mixture of OH·CPh$_2$·CHEt·OH and OH·CHPh·CPhEt·OH. (**I**) or (**II**) with BzCl yields *α-benzoyloxy-α-benzoylpropane*, an oil. With (**I**) *p*-NO$_2$·C$_6$H$_4$·COCl gives *β-keto-α*-p-*nitrobenzoyloxy-α-phenylbutane*, m.p. 57·5—58·5°, whilst with (**II**) the product is *α*-p-*nitrobenzoyloxy-α-benzoylpropane*, m.p. 97—98°. (**II**) and AcCl give a mixture of COEt·CHPh·OAc and COPh·CHEt·OAc. R. T.

Synthesis of 3-*p*-hydroxyphenylcyclohexanone. D. K. Banerjee (*J. Indian Chem. Soc.*, 1940, **17**, 573—577).—Et γ-anisoylbutyrate (*semicarbazone*, m.p. 120—121°) with Zn and CH$_2$Br·CO$_2$Et in C$_6$H$_6$ yields *β-hydroxy-α-carbethoxy-β-p-methoxyphenylpentane-ε-carboxylic acid lactone*, b.p. 229—230°/4 mm., reduced (Zn + NaOH) to *β*-p-*methoxyphenylpimelic acid*, m.p. 154—156°. The *Me*$_2$, b.p. 190—193°/4—5 mm., or *Et*$_2$ ester, b.p. 199—201°/4—5 mm., of this is cyclised (Na in C$_6$H$_6$) to a product hydrolysed (20% H$_2$SO$_4$) to the *Me ether*, m.p. 83° (*semicarbazone*, m.p. 217—219°), of 3-p-*hydroxyphenyl*cyclo*hexanone*, m.p. 159—161°. A. Li.

Sympathomimetics. I. Naphthalene series. S. Rajagopalan (*J. Indian Chem. Soc.*, 1940, **17**, 567—572).—Hydrolysis (dil. HCl) of 1- and 2-C$_{10}$H$_7$·CH(OH)·CH$_2$·NHAc yields 1-(*hydrochloride*, m.p. 156—157°; *picrate*, decomp. 185°) and 2-C$_{10}$H$_7$·CH(OH)·CH$_2$·NH$_2$ (*hydrochloride*, decomp. 180—183°; *picrate*, decomp. 191—192°), respectively. 4 : 1-OMe·C$_{10}$H$_6$·CO·CH$_2$I with piperidine in C$_6$H$_6$ yields 4-methoxypiperidinoaceto-1-naphthone (*hydrochloride*, decomp. 233—234°; *picrate*, decomp. 150°), which could not be demethylated. *ω-Iodo-5-acetoacenaphthone*, m.p. 112—114° (from the Cl-ketone and NaI in COMe$_2$), yields with (CH$_2$)$_6$N$_4$ an additive *compound*, m.p. 160°, hydrolysed (EtOH–HCl) to ω-amino- (*picrate*, decomp. 147—150°), and with piperidine ω-piperidino-5-acetoacenaphthone (*hydrochloride*, decomp. 235—237°; *picrate*, decomp. 152°). 4-Methoxy-1-naphthacylphthalimide is hydrolysed (conc. HCl at 160—170° under pressure) to 4-hydroxy-ω-aminoaceto-1-naphthone, m.p. 154—155° (picrate, m.p. 186—187°), also obtained from the *N*-Ac (**I**) or *N*-Bz derivative. (**I**) is reduced (Na–Hg) to *β-hydroxy-4-methoxy-β-1-naphthylacetethylamide*, m.p. 155—156°, which could not be hydrolysed. *β-1-Naphthylethylphthalimide*, m.p. 143° {from C$_{10}$H$_7$·[CH$_2$]$_2$·Br and C$_6$H$_4$(CO)$_2$NK in EtOH}, is hydrolysed (conc. HCl under pressure) to 1-C$_{10}$H$_7$·[CH$_2$]$_2$·NH$_2$ (hydrochloride, decomp. 244—245°). Br·[CH$_2$]$_2$·NH$_2$,HBr with the acid chlorides and aq. Na$_2$CO$_3$ yields *β-bromoethyl-α-naphtho-*, m.p. 94°, and *-benzenesulphon-amide*, m.p. 58°. These or Br·[CH$_2$]$_2$·NHBz with α-C$_{10}$H$_7$·OMe and AlCl$_3$ in PhNO$_2$ yield only (C$_{10}$H$_6$·OMe-4)$_2$. *β*-4-Ethoxy-1-naphthylethyl alcohol [from 4 : 1-OEt-C$_{10}$H$_6$·MgBr and (CH$_2$)$_2$O in Et$_2$O] (*picrate*, m.p. 104—105°) yields with PBr$_3$ the bromide, which gives *β*-4-*ethoxy*-1-*naphthylethylphthalimide* (poor yield), m.p. 175°, and with (CH$_2$)$_6$N$_4$ yields an *additive compound*, decomp. 189°. 3 : 4-Dimethoxy-ω-benzamidoaceto-1-naphthone, from 1 : 2-C$_{10}$H$_6$(OMe)$_2$ and NHBz·CH$_2$·COCl in CS$_2$, has m.p. 261—262°. The Na salt (**II**) of *N-benzenesulphonylhomoveratrylamide*, m.p. 89°, with 4 : 1-OMe·C$_{10}$H$_6$·CO·CH$_2$I in EtOH gives a product, hydrolysed (conc. HCl at 170—180°) to the hydrochloride, decomp. >180°, of *N*-4-hydroxy-1-naphthacyl-3 : 4-dihydroxyphenylethylamine (*picrate*, decomp. 189—191°). *ω-Benzenesulphonamidoaceto*-1- and -2-*naphthone* have m.p. 121° and 165°, respectively. Hydrolysis (dil. HCl) of (**I**) yields the *hydrochloride*, decomp. 204°, of 4-methoxy-ω-aminoaceto-1-naphthone (*picrate*, decomp. 191°; *N-PhSO$_2$* derivative, m.p. 147°). 1-C$_{10}$H$_7$·[CH$_2$]$_2$·Br with (**II**) in EtOH yields *N-β-1-naphthylethyl-N-homoveratrylbenzenesulphonamide*, m.p. 82—83°. 1-C$_{10}$H$_7$·MgBr with α-C$_{10}$H$_7$·CO·CH$_2$·NH$_2$,HCl in Et$_2$O yields *β*-hydroxy-*ββ*-1 : 1′-dinaphthylethylamine (*hydrochloride*, decomp. 260°; *picrate*, decomp. 168°). A. Li.

Two ketones of the stilbœstrol group. (Mrs.) R. Jaeger and (Sir) R. Robinson (*J.C.S.*, 1941, 744—747; cf. A., 1939, II, 312).—*p*-ClN$_2$·C$_6$H$_4$·CH$_2$·CO$_2$H and aq. CuSO$_4$–KCN at 50° afford *p*-CN·C$_6$H$_4$·CH$_2$·CO$_2$H, m.p. 152°, converted through the chloride, m.p. 91—92°, and PhOMe–AlCl$_3$–PhNO$_2$ at room temp., then at 60°, into *4-cyano-4′-methoxydeoxybenzoin*, m.p. 116—117°, b.p. 212—214°/0·2 mm. (2 : *4-dinitrophenylhydrazone*, m.p. 212°), converted by EtI–NaOEt–EtOH into *4-cyano-4′-methoxy-α-ethyldeoxybenzoin* (**I**), m.p. 60—62°, b.p. 202—205°/0·3 mm., and thence (MgEtBr–Et$_2$O) γ-p-*anisyl*-4-p-*cyanophenylhexan-γ-ol* (**II**), b.p. 192—198°/0·2 mm. (**II**) and HCl–MeOH give an ester, hydrolysed (10% aq. KOH) to *4-methoxy-αβ-diethylstilbene-4′-carboxylic acid*, m.p. 167°. (**II**) and aq. KOH–EtOH at 165° (sealed tube) yield γ-p-*anisyl*-p-*carboxyphenylhexan-γ-ol*, m.p. 142°. (**II**) and MgMeBr afford a product and thence (Girard's reagent T–EtOH–AcOH) 4-*methoxy-4′-acetyl-αβ-diethylstilbene*, b.p. 162—172°/0·4 mm. (2 : 4-dinitrophenylhydrazone, m.p. 102°), demethylated by HBr (*d* 1·5)–AcOH at 170° to the 4-*OH*-compound, b.p. 202—206°/0·2 mm. (**I**) and MgMeBr give *4-methoxy-4′-acetyl-α-methyl-β-ethylstilbene*, b.p. 191—194°/0·3 mm. (2 : 4-dinitrophenylhydrazone, m.p. 115°). The 4-*OH*-compound, b.p. 210—218°/0·4 mm. (*acetate*, m.p. 102°), and MgMeBr give a mixture, b.p. 190—198°/0·3 mm., probably of 4-hydroxy-4′-α-hydroxy*iso*propyl-α-methyl-β-ethylstilbene and the *iso*propenyl derivative obtained by dehydration. Biological tests are recorded (see A., 1942, III, 132). A. T. P.

Identity of Hinsberg's *o*-trisulphidobenzoic thioanhydride with Smiles and McClelland's 2-dithiobenzoyl. A. Schönberg and (Miss) A. Mostafa (*J.C.S.*, 1941, 793).—2-Dithiobenzoyl, m.p. 77° (Smiles *et al.*, *J.C.S.*, 1922, **121**, 86), is identical with the product of Hinsberg (A., 1910, i, 553). A. T. P.

Kinetics of the nitration of anthraquinone derivatives. R. Oda and U. Ueda (*Bull. Inst. Phys. Chem. Res. Japan*, 1941, **20**, 335—342).—The velocity of reaction of anthraquinone derivatives with H$_2$SO$_4$–HNO$_3$ is a max. with 90% H$_2$SO$_4$. Vals. of *k* of the following compounds are in a descending scale : 1 : 2-benz-, 1-hydroxy-, 2-hydroxy-, 1-chloro-anthraquinone, anthraquinone, anthraquinone-2-carboxylic acid, and 2-chloroanthraquinone. J. L. D.

IV.—STEROLS AND STEROID SAPOGENINS.

Œstrone azobenzene-4-carboxylate. F. Bergel and A. Cohen (*J.C.S.*, 1941, 795—796).—Œstrone (**I**) and azobenzene-4-carboxyl chloride in C$_5$H$_5$N at 50° afford *œstrone azobenzene-4-carboxylate*, m.p. 226·5—227·5°, which with 2% KOH–EtOH yields (**I**), m.p. 259·5—260·5°. M.p. of various samples of (**I**) are recorded. A. T. P.

Subsidiary sterols of yeast. VI. Cryptosterol. H. Wieland and E. Joost (*Annalen*, 1941, **546**, 103—119).—Cryptosterol (**I**) readily adds HCl in dry CHCl$_3$ forming the *hydrochloride* (**II**), C$_{30}$H$_{51}$OCl, m.p. 168—170°, [α]$_D^{20}$ +43·2° in CHCl$_3$, transformed by moist Ag$_2$O in MeOH–C$_6$H$_6$ into *cryptostenediol*, C$_{30}$H$_{52}$O$_2$, m.p. 161—163°, [α]$_D^{20}$ +38·2° in CHCl$_3$, which is oxidised (CrO$_3$ in AcOH at 40—45°) to *cryptostenedione* (**III**), m.p. 154—156°, [α]$_D^{22}$ −0·58° in CHCl$_3$. (**III**) and N$_2$H$_4$,H$_2$O in boiling abs. EtOH give a *product*, C$_{30}$H$_{48}$N$_2$, m.p. 282—284° (decomp.), which must contain the heterocyclic ring —C<C·C / N·N>C— or ·C<C···C / N·N>C· according as the CO groups of (**III**) are in the 1 : 3 or 1 : 4 positions to one another. The absence of enolic reactions from (**III**) is evidence against the first possibility, and this view is confirmed by the observation that (**II**) and KOH–EtOH do not regenerate (**I**) but yield an isomeric substance, *iso*cryptosterol, m.p. 154° (*acetate*, m.p. 159—161°, [α]$_D^{22}$ +33·7° in CHCl$_3$). It appears therefore that the active double linking of (**I**) is in the *βγ*-position to the alcoholic OH. Oxidation (CrO$_3$ in AcOH at 45—55°) of (**II**) gives the Cl-ketone, m.p. 130—133° (A., 1937, II, 243). Oxidation of dihydrocryptosterol (**IV**) (CrO$_3$ in AcOH) at 70° gives small

amounts of a *compound*, $C_{30}H_{48}O_2$, m.p. 144—146°, in which it is probable that >CH·OH has been oxidised to CO and CH_2 vicinal to the passive double linking has been converted into CO. The substance does not give a yellow colour with $C(NO_2)_4$ and the Liebermann reaction is much less pronounced than with (I). Oxidation at a somewhat higher temp. leads to a yellow neutral *substance*, $C_{30}H_{46}O_3$, m.p. 102—103°, apparently a triketone, isolated through the *semicarbazone*, m.p. 252—254° (decomp.), and converted by boiling KOH–MeOH into an isomeric *compound*, m.p. 231—232°. These transformations closely resemble those of quinovic acid. The chromophore in both is the system ·CO·C:C·CO· and the max. in the ultra-violet spectrum of both compounds is almost exactly at the same λ (268 mμ.). The alcohols $C_{30}H_{50}O$ appear generally more closely related to the triterpenes than to the sterols as shown by the characteristic differences in the colour reactions, particularly that of Liebermann and Burchard, and the very differing products of their dehydrogenation by Se. Further, oxidation yields acids of lower mol. wt. the composition of which calls into question the union of OH at $C_{(3)}$. Thus the by-products of the oxidation of (IV) contain an *acid*, $C_{26}H_{38}O_2$ or $C_{27}H_{40}O_2$, m.p. 195° (*Na* salt), which does not give a yellow colour with $C(NO_2)_4$ or the Liebermann–Burchard reaction. This has lost the O of the OH originally present, indicating (with caution) that it was present in the side-chain of (I). Also one of the four rings appears to have become aromatic. Similarly cryptosteryl benzoate yields an acid, $C_{29}H_{43}O_4$·OBz or $C_{28}H_{41}O_4$·OBz, analysed as the *Me* ester, m.p. 191—192° from C_6H_6–MeOH or m.p. 190—199° from EtOAc, which is saturated towards $KMnO_4$, Br, or $C(NO_2)_4$. Acid or ester is hydrolysed to the *hydroxydiketocarboxylic acid*, $C_{28}H_{42}O_5$, m.p. 201—203° (*Me* ester, m.p. 176—177°), which is oxidised to a *(CO)$_3$-acid*, $C_{23}H_{40}O_5$ (*Me* ester, m.p. 155°), obtained also in very small yield from the products of the direct oxidation of (I). The results indicate the possible presence of a side-chain :C:CHMe or CMe:CH_2 in (I) and a near relationship to the isomeric lupeol. Oxidation (OsO_4 and H_2O_2) of (I) affords a 20% yield of an *acid* (V), $C_{25}H_{40}O_3$ (possibly $C_{24}H_{38}O_3$), m.p. 260—261°, $[\alpha]_D$ +51·8° in $CHCl_3$ (*Me* ester, m.p. 154—155°), which is saturated towards $KMnO_4$ and $C(NO_2)_4$ and gives a yellow Liebermann reaction. In more conc. solution an *acid*, $C_{26}H_{42}O_3$, m.p. 150—152,° is produced. The neutral portions of the oxidation product contain a *substance*, $C_{29}H_{48}O_2$ or $C_{30}H_{50}O_2$, m.p. 138—140° (*semicarbazone*, m.p. 190—195°). Oxidation of lanosterol gives an acid very probably identical with (V). Ozonisation of (I) affords (V). Distillation of (III) with B_2O_3 at 340—360°/0·02 mm. yields *cryptostadiene*, $C_{30}H_{50}$, m.p. 141—142°, unsaturated towards $KMnO_4$ and $C(NO_2)_4$ and converted by $KMnO_4$ in AcOH into an isomeric *hydrocarbon*, m.p. 69—70°.

H. W.

21-Aldehydes of the *cyclo*pentanopolyhydrophenanthrene series.—See B., 1941, III, 345.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Camphane series. VI. Synthesis of homocamphoronic acid. P. C. Guha, K. S. Subramanian, and V. R. Srinivasan (*J. Indian Inst. Sci.*, **23**, **A**, 191—200).—$CHMe_2Br·CO_2Et$, Et lævulate, and Zn give a mixture of the Et esters of β-hydroxy-αaβ-trimethyladipic acid and its lactone. The Et ester of the OH-acid with HBr affords the lactonic acid [*Pb* salt, m.p. 165—176° (decomp.); *Cu* salt]. The lactonic ester with KCN followed by H_2SO_4–EtOH yields Et homocamphoronate, which is hydrolysed (HCl) to the acid, identical with a specimen obtained by oxidation (HNO_3) of αα-dibromocamphor.

F. R. S.

Utilisation of Indian turpentine oils. I. Constituents of turpentine oil from *Pinus longifolia*, Roxb., *P. excelsa*, *P. khasya*, and *P. merkussi*. II. Conversion of α- and β-pinenes into bornyl acetate by acetic acid in presence of catalysts. III. (1) Catalytic isomerisation of α-pinene and β-pinene to camphene. (2) Synthesis of camphor from pinene–camphene mixture. P. C. Guha and A. N. Roy (*J. Indian Inst. Sci.*, **23**, **A**, 201—207, 208—216, 217—225).—I. The content of α- (I) and β-pinene (II) in *P. longifolia*, *P. excelsa*, *P. khasya*, and *P. merkussi* is respectively 40%, 87·0%, 95·7%, and 97·9%.

II. In presence of AcOH, Ac_2O, and B_2O_3 the yield of borneol from (I) is 17·5% and from (II) is 18·8%; when small amounts of H_2SO_4 are added, the yields at 50—55° are respectively 35·7% and 24·7%.

III. (1) The isomerisation of pure (I) and mixtures of (I) and (II) to camphene in presence of a no. of catalysts has been studied; the best results are obtained by the use of Sb_2O_3–H_2O–H_2O_2 (40—45% yield). (2) The oxidation of borneols to camphor is best effected with 50% HNO_3–50% H_2SO_4.

F. R. S.

Magnetic susceptibility and optical rotatory powers of 4-hydroxy-α-naphthyliminocamphor. M. Singh and A. Singh (*J. Indian Chem. Soc.*, 1940, **17**, 604—606).—The two forms, light orange (I) and red (II), of 4-hydroxy-α-naphthyliminocamphor have susceptibilities of 6·46 and 6·58 × 10^{-7}, respectively. Mol. structures of (I) and (II) accounting for this difference are proposed. (I) shows mutarotation in NH_2Ph, MeOH, and EtOH, the final [α] [temp. ?] equalling that of (II).

D. F. R.

Terpene thiocyanocarboxylic esters.—See B., 1941, II, 418.

Reaction of hydrogenation and dehydrogenation through disproportionation of hydrogen in abietic acid. T. Hasselstrom, E. A. Brennan, and S. Hopkins, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 1759—1760).—Steele's abietic acid or gum or wood resin with 1—2% of I at 160—170° gives de- and di-hydroabietic acid, isolated as the 6-sulphonic acid, $+3H_2O$, and as hydroxytetrahydroabietolactone, respectively.

R. S. C.

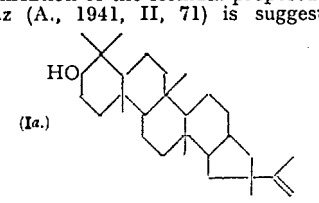
Surface films of lupane derivatives. P. Bilham, E. R. H. Jones, and R. J. Meakins (*J.C.S.*, 1941, 761—766).—The small limiting area vals. observed in surface-film measurements, particularly with bisnorlupanic acid and ψ-lupenol, and the large area vals. with lupenediol and lupanetriol monoacetate, in conjunction with chemical data, furnish evidence that in lupeol the ·CMe:CH_2 group is situated at the opposite extremity of the ring system to the OH.

F. R. S.

Constitution of β-boswellic acid. J. C. E. Simpson and G. A. R. Kon (*J.C.S.*, 1941, 793—794).—α-Boswellic acid heated at 340° with Cu gives nor-β-boswellenone, indicating that migration of the double linking does not take place. Pyrolysis of the acid and its Ac derivative affords β-boswellyene. These experiments cannot be regarded as conclusive evidence against Simpson and Williams' formula for the acid (A., 1938, II, 500).

F. R. S.

Constitution of lupeol. E. R. H. Jones and R. J. Meakins (*J.C.S.*, 1941, 757—761).—The non-reactivity of the CO and CO_2H group in norlupanonol and bisnorlupanolic acid respectively indicates that the ·CMe:CH_2 group in lupeol (**Ia** or *b*) is attached to a quaternary C of the polycyclic system, and a modification of the formula proposed by Ruzicka and Rosenkranz (A., 1941, II, 71) is suggested: (**Ia**) is preferred.



(Ia.) (Ib.)

Reduction of lupenone by N_2H_4 and NaOEt at 190° gives an improved yield (96%) of α-lupene, which with OsO_4 affords *lupanediol*, m.p. 242—245°, $[\alpha]_D^{20}$ +5·1° in C_5H_5N, oxidised [$Pb(OAc)_4$] to *norlupanone*, m.p. 172—173°, $[\alpha]_D^{20}$ −18·4° (*c* = 1·72). This ketone is reduced [$Pr^{\beta}OH$–$Al(OPr^{\beta})_3$] to *norlupanol*, m.p. 160—161° [*acetate*, m.p. 166—167°, $[\alpha]_D^{20}$ −22·4° (*c* = 0·41)]. Reduction [$Pr^{\beta}OH$–$Al(OPr^{\beta})_3$] of lupenal yields *ψ-lupenol*, m.p. 167—168°, $[\alpha]_D^{20}$ −6·50° (*c* = 1·84) [*acetate*, m.p. 107·5°, $[\alpha]_D^{20}$ −2·9° (*c* = 1·84)], and similar reduction of lupenalyl acetate gives *lupenediol*, m.p. 231—232°, $[\alpha]_D^{20}$ −3·5° in C_5H_5N [*monoacetate*, m.p. 240—241°, $[\alpha]_D^{20}$ +7·2° (*c* = 2·17); *diacetate*, m.p. 163—164° $[\alpha]_D^{20}$ +9·7° (*c* = 1·89)]. Lupenyl acetate and OsO_4 give *lupanetriol monoacetate*, m.p. 259—262°, $[\alpha]_D^{20}$ +12·4° (*c* = 1·76).

F. R. S.

VI.—HETEROCYCLIC.

Amidine sulphanilamides.—See B., 1941, III, 344.

Kostanecki–Robinson reaction. III. Benzoylation of orc-acetophenone and its monomethyl ether. S. M. Sethna and R. C. Shah (*J. Indian Chem. Soc.*, 1940, **17**, 601—603).—

Benzoylation of orcacetophenone (**I**) gives *7-benzoyloxy-3-benzoyl-5-methylflavone*, m.p. 172—173°, which with H_2SO_4 gives the 7-*OH*-compound, m.p. 282—283° (*Ac* derivative, m.p. 171—173°; *Me ether*, m.p. 186—187°), further converted by KOH–EtOH into 7-hydroxy-5-methylflavone, m.p. 312° (lit. 297°) [Me ether, m.p. 122—123° (lit. 115°)]. The Me ether of (**I**) gives on benzoylation a similar series of compounds, identical with those described previously.

F. R. S.

Chemistry of evodionol. F. N. Lahey (*Univ. Queensland Papers*, 1941, **1**, No. 17, 1—10).—Evodionol (**I**) (cf. B., 1940, 494), new formula $C_{14}H_{16}O_4$, m.p. 86° [*Ac* derivative, m.p. 66°; 2 : 4-dinitrophenylhydrazone, m.p. 221°; $(NO_2)_2$-derivative, m.p. 156°] with H_2–Pt–EtOH gives *dihydroevodionol*, m.p. 69°, and with Me_2SO_4–aq. KOH gives *methylevodionol* (**II**), m.p. 79° (2 : 4-*dinitrophenylhydrazone*, m.p. 157°), which with H_2–Pt–EtOH gives *dihydromethylevodionol*, m.p. 91°. Oxidation of (**II**) ($KMnO_4$–$COMe_2$) gives an acid (**III**), $C_{13}H_{16}O_4(CO_2H)_2$, m.p. 134°, converted by boiling MeOH–H_2SO_4, not into its ester, but into the *ester*, m.p. 76° (2 : 4-*dinitrophenylhydrazone*, m.p. 147°), of an *acid*, $C_{13}H_{17}O_4{\cdot}CO_2H$, m.p. 116°, also obtained by boiling (**III**) with 2% aq. H_2SO_4. With KOBr at 20—30°, (**III**) gives CBr_4 and an *acid*, $C_{11}H_{13}O_3Br_2{\cdot}CO_2H$, m.p. 125°, converted by Na–Hg–H_2O into an *acid*, $C_{11}H_{16}O_2{\cdot}CO_2H$, m.p. 74°, which gives on distillation with soda-lime a small yield of a (?) trimethoxymethylbenzene *derivative* (**IV**), m.p. 54°. At 140—150° (**III**) gives CO_2, AcOH, an *acid*, $C_{10}H_{13}O_2{\cdot}CO_2H$, m.p. 184°, and a phenolic *acid*, which at 250° gives a small yield of product giving (**IV**) with Me_2SO_4. With KOBr at 5—10° (**III**) gives an *acid*, $C_{11}H_{14}O_3(CO_2H)_2$, m.p. 163°, and $CHBr_3$. It is established that *paeonoxyacetic acid*, $C_{11}H_{12}O_5$, m.p. 133° (prepared by boiling paeonol, $CH_2Br{\cdot}CO_2Et$, K_2CO_3, and $COMe_2$ and hydrolysing the ester by boiling with EtOH–KOH), with KOBr at 20—30° gives CBr_4 + an *acid*, $C_8H_7O_2Br(CO_2H)_2$, m.p. 238° converted by Na–Hg–H_2O into an *acid*, m.p. 150° (not containing Br), and that $CH_2Ph{\cdot}CO_2H$ gives an *acid*, $C_7H_6OBr{\cdot}CO_2H$, m.p. 159°.

T. F. W.

Thiophen series. LVII. α-Polythienyls. W. Steinkopf, R. Leitsmann, and K. H. Hofmann [with, in part, H. F. Schmitt and R. Schaller] (*Annalen*, 1941, **546**, 180—199; cf. A., 1937, II, 163).—The considerably higher m.p. of the polyphenyls (**I**) shows that they are relatively more saturated than the polythienyls (**II**). The empirical rule that 5—6 aliphatic double linkings are necessary for the development of colour in compounds which otherwise contain no chromophoric groups can be extended to (**II**), in which terthienyl with 6 double linkings is feebly coloured and the colour deepens with increasing no. of double linkings. The bathochromic action of the aliphatic double linking is somewhat more pronounced than that of the similar linking of (**II**). All (**II**) afford typical halochromic phenomena with conc. H_2SO_4 or $CCl_3{\cdot}CO_2H$, wherein they resemble the diphenylpolyenes and differ from (**I**). 2-Iodothiophen (**III**) is treated with Cu powder at 190° and then at 200—210°, and the product after removal of unchanged (**III**) and dithienyl in steam is submitted to fractional sublimation in a high vac., thereby giving *tri-* (**IV**), m.p. 94—95°, *tetra-*, m.p. 207—208°, *penta-* (**V**), m.p. 252—253°, and *hexa-* (**VI**), m.p. 304°, *-2-thienyl*. Dropwise addition of Br in CS_2 to (**IV**) in the same solvent leads to 1 : 8-*dibromo-*, m.p. 155—156°, converted by an excess of Br into *octabromo-*, m.p. 268—269°, *-2-trithienyl*. $HgCl_2$ and NaOAc in aq. EtOH at room temp. transform (**IV**) into 1-*chloromercuri-*, m.p. 296—298° (darkening), and 1 : 8-*dichloromercuri-*, m.p. >320°, *-2-trithienyl*, converted by I–aq. KI into 1-*iodo-*, (**VII**), m.p. 146—148°, and 1 : 8-*di-iodo-* (**VIII**), m.p. 198—200°, *-2-trithienyl*. Exposure of (**V**) to Br vapour affords *dodecabromo-2-pentathienyl*, m.p. 337—338°. (**VI**) is also obtained from 5 : 5′-diiodo-2 : 2′-dithienyl and Cu-bronze or from a mixture of (**VII**) and (**VIII**) with Cu at 250°. Br vapour and (**VI**) give *tetradecabromo-2-hexathienyl*, m.p. 368—369°. *2-Heptathienyl*, m.p. 326—328°, is obtained from (**III**) and 2 : 5-diiodothiophen in presence of Cu-bronze. Treatment of (**III**) and 5-iodo-2-thiotolen with Cu-bronze at 180° and then at 200° followed by distillation of the product with steam and treatment of the solid portion of the distillate with $HgCl_2$ leads to the isolation of 5 : 5′-dichloromercuri- and 5′-*chloromercuri-5-methyl-* (**IX**), softens without definite melting at ~225°, *-2 : 2′-dithienyl*, transformed by dil. HCl at 100° into 5-*methyl-2 : 2′-dithienyl* (**V**), b.p. 145—146°/17 mm., and by I–KI into 5-*iodo-5′-methyl-2 : 2′-dithienyl* (**XI**), m.p. 87—88°. Successive action of (**XI**) and CO_2 on MgEtBr in Et_2O at 0° affords *5-methyl-2 : 2′-dithienyl-5′-carboxylic acid*, m.p. 197—198° (*Me* ester, m.p. 112°). Passage of Cl_2 through (**X**) in AcOH leads to 3 : 4′ : 3′ : 4′ : 5′-*pentachloro-5-methyl-2 : 2′-dithienyl*, m.p. 111—112°. The 3 : 4 : 3′ : 4′ : 5′-Br_5-compound, m.p. 170—171°, is obtained by use of Br in CS_2 and is converted by an excess of Br into 3 : 4 : 3′ : 4′ : 5′-*pentabromo-5-bromomethyl-2 : 2′-dithienyl*, m.p. 264°. (**III**) and (**XI**) with Cu-bronze at 200° followed by $HgCl_2$–NaOAc yield 8-*chloromercuri-1-methyl-2-trithienyl*, m.p. 235—236° after softening, transformed by boiling dil. HCl into 1-*methyl-2-trithienyl*, m.p. 90—91°. An improved method is described for the prep. of 1 : 10-dibromo-2-tetrathienyl, m.p. 251° (lit. m.p. 248°). 1 : 10-*Dimethyl-2-tetrathienyl* has m.p. 184—185°. 5-Iodo-2-phenyl- (**XII**) and 2 : 5-di-iodo- (**XIII**) -thiophen and Cu-bronze at 200° afford 5 : 5-diphenyl-2 : 2′-dithienyl and 1 : 8-*diphenyl-2-trithienyl*, m.p. 273°. (**III**) and (**XII**) similarly give *5-phenyl-2 : 2′-dithienyl*, m.p. 119°. With different proportions (**XII**), (**XIII**), and Cu-bronze at 280° yield 1 : 10-*diphenyl-2-tetrathienyl*, m.p. 317°. Treatment of tetraiodothiophen with $ClSO_3H$ leads to *tetrachlorohexaiodo-2-tetrathienyl*, m.p. 218—220°, converted by Cl_2 in boiling CS_2 into *decachloro-2-tetrathienyl*, m.p. 246—247°; the corresponding Br_{10}-compound, m.p. 326—328°, is derived from hexabromo-2 : 2′-dithienyl and $ClSO_3H$. Addition of 3 : 4-dibromothiophen-2 : 5-dialdehyde to MgPhBr in Et_2O gives 3 : 4-*dibromo-2 : 5-dihydroxybenzylthiophen*, m.p. 161°, transformed by HBr–AcOH to 3 : 4-*dibromo-2 : 5-dibromobenzylthiophen*, m.p. 123—124°, which with Cu-bronze in boiling C_6H_6 affords cyclo-*di*-3 : 4-*dibromodiphenylthioxal*, $\left[\begin{matrix}CBr{:}C(CHPh)\\CBr{:}C(CHPh)\end{matrix}\!\!>\!S\right]_3$, m.p. 250—255°.

H. W.

Thiophen series. LVIII. Di- and tri-ethylthiophen. W. Steinkopf, H. Frömmel, and J. Leo (*Annalen*, 1941, **546**, 199—204).—2-Acetylthiophen and $N_2H_4H_2O$ at 150° give the hydrazone, transformed by NaOEt in abs. EtOH at 160—170° into 2-ethylthiophen, b.p. 130—133°, in 60% yield; this is converted by AcCl and $SnCl_4$ in thiophen-free C_6H_6 at >10° into 5-*acetyl-2-ethylthiophen*, b.p. 121—123°/13 mm. (p-*nitrophenylhydrazone*, m.p. 194—195·5°); the corresponding hydrazone and NaOEt in EtOH yield 2 : 5-*diethylthiophen*, b.p. 63—66°/14 mm., with some 2 : 5 : 2′ : 5′-*tetraethyl-3 : 3′-dithienyl*, b.p. 195°/14 mm. 3-Acetyl-2 : 5-diethylthiophen (*semicarbazone*, m.p. 167° after softening) is transformed through the hydrazone into 2 : 3 : 5-*triethylthiophen*, b.p. 104—107°/15 mm., in 55% yield. $CHEtBr{\cdot}CO_2Et$ is converted by Cu powder at 190° and then at 215° into $(CHEt{\cdot}CO_2Et)_2$, b.p. 215—247°, hydrolysed by HBr (*d* 1·78) at 145—150° to a mixture of the *dl-* and *meso*-forms of αβ-diethylsuccinic acid. The corresponding dry Na salts when distilled with P_2S_3 affords 3 : 4-*diethylthiophen* (**I**), b.p. 185—187°. This is transformed by $HgCl_2$ and NaOAc in aq. EtOH into 2 : 5-dichloromercuri-, m.p. 259°, with some 2-*chloromercuri-*, m.p. 118°, -3 : 4-*diethylthiophen*. This with NaI in $COMe_2$ affords *Hg* 3 : 4 : 3 : 4′-*tetraethyl-2 : 2′-dithienyl*, m.p. 93°. (**I**), AcCl, and $TiCl_4$ in thiophen-free C_6H_6 at >15° yield 2-*acetyl-3 : 4-diethylthiophen*, b.p. 128—130°/12·5 mm. (p-*nitrophenylhydrazone*, m.p. 140°).

H. W.

Thiophen series. LIX. Derivatives of dibenzthiophen resembling atophan. W. Steinkopf and H. Engelmann (*Annalen*, 1941, **546**, 205—208).—Derivatives of dibenzthiophen are darker than their Ph_2 analogues and paler than the corresponding dithienyl compounds. 3-Acetyldibenzthiophen, isatin, and 28% KOH at 105° yield 3-4′-*carboxy-2′-quinolyldibenzthiophen*, decomp. 299—300°, converted by distillation with soda-lime into 3-2′-*quinolyldibenzthiophen*, m.p. 144—145°. Similarly, 3 : 6-diacetyldibenzthiophen gives 3 : 6-*di-4′-carboxy-2′-quinolyldibenzthiophen* (**I**), amorphous, decomp. 330—340°, orange-red form (**II**) by acidification of an alkaline solution by dil. AcOH or yellow form (**III**) by passing CO_2 into the ammoniacal solution. (**III**) passes into (**II**) when heated or boiled with EtOH without undergoing chemical decomp. (**I**) is decarboxylated to 3 : 6-*di-2′-quinolyldibenzthiophen*, m.p. 206—207°.

H. W.

Thiophen series. LX. Deuterothiophen. W. Steinkopf and M. Boëtius (*Annalen*, 1941, **546**, 208—210).—Cautious distillation of *tetrachloromercurithiophen* with 18% DCl yields *tetradeuterothiophen*, b.p. 82·8—83·3°/748 mm., m.p. −38·83° to −38·54°; thiophen has b.p. 83·3—83·7°/747·5 mm., m.p. −39·82° to −39·62°.

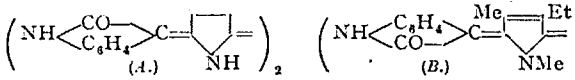
H. W.

Derivatives of thioxanthen. C. V. T. Campbell, A. Dick, J. Ferguson, and J. D. Loudon (*J.C.S.*, 1941, 747—750).—Condensation (NaOH) of 2 : 4-$(NO_2)_2C_6H_3$·CHO with *p*-C_6H_4Me·SH gives 4-*nitro*-2-(p-*tolylthio*)*benzaldehyde* (**I**), m.p. 147° (*oxime*, m.p. 164°), and a smaller amount of the 2-*nitro*-4-compound, m.p. 109° (*oxime*, m.p. 108°); 4-*nitro*-2-(β-*naphthylthio*)*benzaldehyde*, m.p. 156—157°, is obtained from β-$C_{10}H_7$·SH. Oxidation (H_2O_2) of these aldehydes leads to 4-*nitro*-2- (**II**), m.p. 217° and 2-*nitro*-4-(p-*toluenesulphonyl*)-*benzoic acid*, m.p. 191°. 5-*Nitro*-2-(p-*tolylthio*)-*benzaldehyde*, m.p. 156°, -*benzoic acid*, m.p. 253°, and-*benzophenone* (**III**), m.p. 102°, are similarly obtained; the last-named is oxidised (H_2O_2) to the *sulphone*, m.p. 184°, which with piperidine affords 5-*nitro*-2-*piperidinobenzophenone*, m.p. 102°. In conc. H_2SO_4, (**I**) is converted into 6-*nitro*-2-*methyl*-*thioxanthone*, m.p. 276°, and -*thioxanthen*, m.p. 155°. Oxidation (H_2O_2) of these products yields 6-*nitro*-2-*methylthioxanthone dioxide*, m.p. 238°, also obtained by cyclisation ($SOCl_2$–$AlCl_3$) of (**II**). Similarly prepared are 6-*nitro*-1 : 2-*benz*-*thioxanthone*, m.p. 273°, and -*thioxanthen*, m.p. 168°, and 7-*nitro*-2-*methyl*-*thioxanthone*, m.p. 262°, and -*thioxanthen*, m.p. 146°, and the *dioxide*, m.p. 287°. Conc. H_2SO_4 and (**III**) give 7-*nitro*-9-*phenyl*-2-*methylthioxanthhydrol*, m.p. 203° (*chloride-ferrichloride*, decomp. 197—200°; *Et ether*, m.p. 151°), converted by HCl–EtOH into the -*methylthioxanthen*, m.p. 167°. F. R. S.

Synthesis of new local anæsthetics. V. K. N. Gaind, J. N. Ray, and B. Sarin (*J. Indian Chem. Soc.*, 1941, **17**, 619—622).—6-Aminoquinoline and CH_2Cl·COCl give 6-ω-*chloroacetamidoquinoline*, m.p. 154°, which condenses with the appropriate base to form 6-ω-*piperidino*-, m.p. 101° (*dihydrochloride*, m.p. 133°), and -NEt_2-compounds, m.p. 86° (*dihydrochloride*, m.p. 250°). In a similar manner, the following substances are prepared: 6-β-*chloro*-, m.p. 178°, 6-β-*piperidino*-, m.p. 67°, and 6-ω-*diethylamino*-*propion*- (*picrate*, m.p. 180°); 8-ω-*chloro*-, m.p. 131°, and 8-ω-*piperidino*-*acet*- [*hydrochloride*, m.p. 77° (decomp.)]; 8-β-*chloro*-, m.p. 88°, 8-β-*piperidino*-, m.p. 108° [*hydrochloride*, m.p. 189° (decomp.)], and 8-β-*diethylamino*-*propion*- (*dipicrate*, m.p. 167°); 5-ω-*chloro*-, m.p. 157°, 5-ω-*piperidino*-, m.p. 62°, and 5-ω-*diethylamino*-*acet*- (*picrate*, m.p. 203°); 5-β-*chloropropion*- [*hydrochloride*, m.p. 226° (decomp.)], and 5-β-*piperidinopropion*-*amidoquinoline* (*dipicrate*, m.p. 230°); 3-ω-*chloro*-, m.p. 203°, 3-ω-*piperidino*-, m.p. 175° (*dihydrochloride*, m.p. 280°), and 3-ω-*diethylamino*-*acet*-, m.p. 99° (*dihydrochloride*, m.p. 232°); and 3-β-*chloro*-, m.p. 228° (decomp.), and -*piperidino*-*propion*-*amidocarbazole*, m.p. 219° (*dihydrochloride*, m.p. 298°). The carbazole derivatives possess potent anæsthetic efficiency as tested on rabbit's cornea. F. R. S.

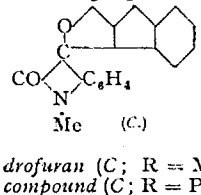
Associating effect of the hydrogen atom. VIII. The N–H–N bond. Benziminazoles, glyoxalines, amidines, and guanidines. L. Hunter and J. A. Marriott (*J.C.S.*, 1941, 777—786).—Measurement of mol. wt. of amidines and related substances in $C_{10}H_8$ over a range of concn. indicates mol. association through N–H–N bonds in those compounds possessing an unsubstituted NH group. From the large factors of association exhibited by the glyoxalines and benziminazoles, it would appear that the N–H–N bond is neither so weak nor so rare as has hitherto been supposed. The strength of the bond is evidently enhanced in compounds of tautomeric character, and the virtual tautomerism of the types mentioned is explained as a resonance phenomenon. The following are described: *N-phenyl*-*N'*-β-*naphthyl*-, m.p. 86°, *NN'-diphenyl*-*N*-*methyl*-, m.p. 83°, N-o-, m.p. 143°, and N-m-*tolyl*-N'-p-*tolyl*-, m.p. 79°, and *NN-diphenyl*-N'-o-*tolyl*-*acetamidine*, m.p. 100°. F. R. S.

Constitution of pyrrole-blue dyes. W. Steinkopf and H. Wilhelm (*Annalen*, 1941, **546**, 211—232).—Cryoscopic and ebullioscopic determinations of the mol. wt. of three dyes of this series in six solvents at widely varied concn. show that contrary to Pratesi (A., 1933, 958) they are formed from 2 mols. of a pyrrole and 2 mols. of an isatin with loss of 2 mols. of H_2O and thus resemble the indophenines. Treatment of 1-methylisatin (**I**), m.p. 132°, with pyrrole in H_2O at room temp. or with Mg pyrryl bromide in Et_2O leads to 3 : 2′-*pyrryl*-1-*methyldioxindole* (**II**), m.p. 158°, in which OH cannot be detected by CH_2N_2; attempted methylation by Me_2SO_4, benzoylation, or acetylation gives a blue dye. Similarly, Mg cryptopyrryl bromide and (**I**) in boiling Et_2O give 3 : 2′-*cryptopyrryl*-1-*methyldioxindole*, m.p. 158° (becomes blue), whereas in boiling C_6H_6 the product is 1-*methylisatin*-[*cryptopyrrole*]-*indophenine*, $C_{31}H_{36}O_2N_4$, m.p. 305°, accompanied by an unidentified *compound*, $C_{25}H_{31}ON_3$, m.p. 202—205°, which gives a very unstable *hydrochloride*. The Grignard compounds from 2 : 3- and 2 : 5-dimethylpyrrole (**III**) and (**I**) yield respectively 3 : 2′-4 : 5′-*dimethylpyrryl*-, becomes blue above 155° and then softens without definitely melting, and 3 : 3′ : 2′ : 5′-*dimethylpyrryl*-, m.p. 212—214°, -1-*methyldioxindole*. The last compound does not give a blue colour when heated or when treated with acids, thus corresponding with the behaviour of (**III**). The remainder can be transformed by AcOH in EtOH into blue dyes identical with those derived directly from (**I**) and the corresponding pyrroles. The formation of pyrrole-blue, like that of the indophenines, proceeds through the 3-2′-pyrryldioxindoles. With a large excess of the Grignard reagent from (**III**) and isatin the product is 3 : 3-*di*-3′-2′ : 5′-*dimethylpyrryloxindole*, m.p. 249° (decomp.). 1-Methylisatin pyrrole-blue dyes yield vats when reduced under definite conditions by Zn dust in C_5H_5N–Ac_2O and when filtered into H_2O 1-*methylisatin*-*cryptopyrrole*-*blue*, m.p. 303—305°, and -2 : 3-dimethylpyrrole-blue are smoothly regenerated. Contrary to Pratesi therefore (*loc. cit.*) the dyes can be vatted. Application of the method to 1-*methylisatin*-[*pyrrole*]-*indophenine*, m.p. 305°, from (**II**) in boiling EtOH–AcOH or from (**I**) and pyrrole in EtOH–AcOH at 75°, 1-*methylisatin*-[*opsopyrrole*]-*indophenine*, m.p. 304°, from (**I**) and opsopyrrole in EtOH–AcOH at 85°, or 1-carbethoxymethylisatin-[pyrrole]-indophenine gives partly acetylated compounds, reconverted into the original dyes by long boiling with C_5H_5N. Acetylation must occur at the NH of the pyrrole ring since the isatin N is attached to Me. In agreement with Pratesi the direct acetylation with Ac_2O and NaOAc has not proved possible. Nevertheless it is established that pyrrole-blue dyes from pyrroles with free α-positions are capable of acetylation. Dyes derived from pyrroles with simple components such as 2 Bz or Bz and CO_2H could not be isolated directly from their components or through the Mg pyrryl halides and are very unstable, if capable of existence. Grignarded indole and 3-methylindole and Bz_2 give compounds regarded for reasons of analogy as ms-3-*indolylbenzoin*, m.p. 114—116° (decomp.), and ms-2 : 3-*methylindolylbenzoin*, m.p. 133° (decomp.); these are very labile and decompose slowly into their components at room temp., immediately in boiling dil. EtOH or when heated in vac. On the other hand, Et 1-acetylisatate and Mg pyrryl iodide give, in poor yield, *Et* o-*acetamido*-α-2-*pyrrylmandelate*, m.p. 124° after becoming blue, which is as stable as the above oxindole derivatives. Mol. wt., acetylatability, colour, sparing solubility, and behaviour in the vat all harmonise with formula (*A*) for the pyrrole-blue dyes. The apparent contradiction caused by the formation of dyes from 2 : 3-dimethyl- and, particularly, from crypto-pyrrole is removed by the observation that they cannot be acetylated, thus leading to the assumption that Me



(*A.*) (*B.*)

has wandered from $C_{(2)}$ to N and that cryptopyrrole-blue is (*B*). Indirect confirmation of this view is found in the observation that Grignarded indole, 2- and 3-methylindole, and (**I**) afford respectively 1-*methyl*-3 : 3′-*indolyldioxindole* (**IV**), m.p. 171—174° (with 1-*methyl*-3 : 3-*di*-3′-*indolyloxindole*, m.p. 292—293°), 1-*methyl*-3 : 3′ : 2′-*methylindolyldioxindole* (**V**), m.p .207—216°, and 1-*methyl*-3 : 2′ : 3′-*methylindolyldioxindole* (**VI**), m.p. 234° after becoming discoloured. These do not yield dyes. This is particularly important with the last-named since it presents a particular case of 2 : 3 : 4-trisubstituted pyrrole in which wandering of Me is excluded. (**V**) and (**VI**) are unchanged by prolonged boiling with Ac_2O but (**IV**) is transformed into an intensely yellow substance regarded as 2-*hydroxy*-2-*methyl*-5 : 5-N-*methylphenylene*-*carbamyl*-3 : 4-2′ : 3′-*indolo*-2 : 5-*dihydrofuran* (*C*; R = Me), m.p. 240° (decomp.); the analogous *compound* (*C*; R = Ph) obtained by BzCl in $COMe_2$–C_5H_5N has m.p. ~240° (decomp.). Further support is given to (*A*) by the existence of a second series of coloured condensation products of isatins and pyrroles with free positions at $C_{(2)}$. Thus opsopyrrole and (**I**) slowly afford 2 : 5-[3-*methyl*-4-*ethyl*-



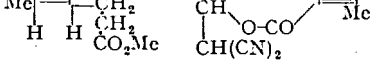
(*C.*)

pyrrolenylene]-*di*-3-1-*methylisatin*, m.p. 211—214°, whilst pyrrole and (I) give 2 : 5-*pyrrolenylenedi*-3-1-*methylisatin*, m.p. ~250° (decomp.). H. W.

New reactions of pyroporphyrins. H. Fischer and E. A. Dietl (*Annalen*, 1941, **547**, 86—102; cf. A., 1938, II, 297).—Pyrohæmin Me ester and $CH_2Cl{\cdot}CO{\cdot}NH_2$–$SnBr_4$ afford 6-*bromopyroporphyrin Me ester*, $C_{32}H_{35}O_2N_4Br$, m.p. 251° (*Zn* complex salt, $C_{32}H_{33}O_2N_4BrZn$, m.p. 242°; *Cu* complex, m.p. 214°), converted by N_2H_4,H_2O–MeOH at 130° into 6-*bromopyroporphyrinhydrazide*, m.p. >330°. 6-Formylpyroporphyrin Me ester gives a *Zn* salt, $C_{33}H_{34}O_3N_4Zn$, m.p. ~210°. Pyroporphyrin Me ester-6-acrylic acid and NH_2OH,HCl–C_5H_5N at 100° (bath) yield the *oxime*, m.p. 255°, of 6-acetylpyroporphyrin Me ester (*Cu* salt, m.p. 239°; *Bz* derivative, m.p. 191°). 6-Hydroxycyanopyroporphyrin and conc. H_2SO_4 (10 min.) give 6-formylpyroporphyrin and (after CH_2N_2) *pyroporphyrin Me ester*-6-*glycollamide* (I) (*Cu* salt, m.p. 235°), oxidised by $KMnO_4$–$COMe_2$ (+C_5H_5N) to the -6-*glyoxylamide*, m.p. 265° (oxime). (I) is hydrogenated (Pd-black; HCO_2H) at 65° to the corresponding -6-*acetamide*, m.p. 302°, converted by H_2SO_4–20% oleum at 50° into the 6-*methylpyrorhodin*, m.p. 278°. A. T. P.

Chlorophyll. CIII. Purpurins. Purpurin 4. M. Strell (*Annalen*, 1941, **546**, 252—272).—Treatment of chlorin e_6 Me_3 ester with 20% HCl for 30 hr. at room temp. essentially causes hydrolysis of the propionic ester group. Similar treatment of purpurin 5 Me_2 ester (I) gives the Me_1 ester with free propionic acid residue. If the action is prolonged CO_2Me at $C_{(6)}$ is gradually hydrolysed and this is followed by lactonisation to "unstable chlorin 5." The stability of CO_2Me at $C_{(6)}$ towards acid is therefore very considerable and in the condensation of purpurin 5 with HCN it is probable that lactonisation is due to elimination of MeOH with previous hydrolysis. Also, hydrolysis of (I) cannot take place during condensation with $CH_2(CN)_2$ but the latter becomes attached to the γ-CHO and lactonisation then leads to "unstable

(II.)



chlorin 4" (II). The lactone constitution is supported by the observation that (II) is isomerised by HI to a porphyrin with extraction no. 12 and spectrum of the type of chloroporphyrin e_5 and further that the behaviour of the Me_1 ester of (II) towards alkali is similar to that of chloroporphyrin e_5-lactone. Treatment of (II) with very dil. alkali causes a change in the spectrum possibly due to conversion of ·CN into :C:NH. The action of $CH_2(CN)_2$ on mesopurpurin 5 Me_2 estef gives "meso-*unstable chlorin* 4" *Me*$_1$ *ester*, m.p. 230°, $[\alpha]^{20}_{red}$ ~+120° on $COMe_2$, also obtained by catalytic hydrogenation of (II) in $COMe_2$, thus showing that the vinyl group of (VI) is intact. A *Cu* salt, $C_{37}H_{34}O_4N_6Cu$, of (II), m.p. >320°, $[\alpha]^{20}_{white}$ +496° ±50° in $COMe_2$, and a *Zn* salt, $C_{37}H_{36}O_4N_6Zn$, of its *meso*-compound, m.p. 210°, $[\alpha]^{20}_{white}$ +2000°±200° in $COMe_2$, are described. Esterification of (II) gives *purpurin Me*$_2$ *ester* (III), $C_{38}H_{38}O_4N_6$, m.p. 186°, $[\alpha]^{20}_{690}$ ~+590°, $[\alpha]^{20}_{white}$ +2980° in $COMe_2$, isomerised by HI to the product derived from (II). Boiling C_5H_5N transforms (III) into a non-cryst. compound with definite chlorin spectrum and extraction no. 15. Hydrogenation in $COMe_2$ leads to the meso-*compound*, m.p. 196°, also obtained by prolonged hydrogenation to the leuco-compound followed by re-oxidation. With cold $CHN_2{\cdot}CO_2Et$ (III) gives a mol. *compound*. Treatment of (III) with KOH–PrOH under the conditions of the neopurpurin reaction gives a small amount of *neopurpurin* 4 and a compound with a well-defined chlorin spectrum. Boiling C_5H_5N transforms (II) or its *meso*-compound into "*substance* 558 mμ." (IV), $C_{38}H_{(38)38}O_4N_6$, m.p. 257°, $[\alpha]^{20}_{white}$ ~+600° in $COMe_2$, or its meso-*analogue*, $C_{38}H_{40(38)}O_4N_6$, m.p. 245°. The spectrum of (IV) is complex and contains 3 bands; it does not resemble that of a chlorin or a purpurin. It cannot belong to the porphyrin series. Attempted isomerisation with HI causes much decomp. and production of rhodoporphyrin in small proportion. Investigations of the action of $CH_2(CN)_2$ on purpurin 5 show that the formation of a purpurin type does not depend on the presence of γ-CO but is generally due to the production of a conjugated double linking in the γ-position. It appears expedient, therefore, to classify as purpurins all compounds containing a conjugated double linking in the γ-position to the chlorin skeleton. Those purpurins which contain CO_2H at $C_{(6)}$ and therefore arise from an "unstable chlorin" are designated "purpurins of the first order" (V), and those which have only H at $C_{(6)}$ are "purpurins of the second order" (VI). (V) are derivatives of rhodochlorin with a conjugated double linking in the γ-side-chain whereas (VI) are derived from pyrrochlorins with a conjugated double linking in the γ-position. Boiling C_5H_5N quantitatively transforms purpurin Me_1 ester into vinylrhodoprophyrin under conditions which cause little change in (I). With each substance a positive reaction is observed with $CH_2(CN)_2$. With both compounds NH_2OH,HCl causes appearance of the chlorin spectrum; the change does not appear to consist of oximation of γ-CHO, but to be a conversion into a complex mixture of chlorins such as is induced by many org. bases. H. W.

Reversible bleaching of chlorophyll.—See A., 1942, I, 69.

***iso*Benzoxazoles [benz*iso*oxazoles]. IV.** W. Borsche and M. Wagner-Roemmich (*Annalen*, 1941, **546**, 273—276; cf. A., 1939, II, 454).—*o*-$C_6H_4F{\cdot}CO{\cdot}NH_2$ is dehydrated by $SOCl_2$ at 100° to *o*-*fluorobenzonitrile* (I), b.p. 90°/21 mm., converted by MgMeI in Et_2O into *o*-*fluoroacetophenone*, b.p. 80—85°/16 mm. (*semicarbazone*, m.p. 193°). Ring-closure of the *oxime*, m.p. 72—74°, to 2-*methylbenziso*oxazole, b.p. 108—110°/16 mm., is effected as easily as that of *o*-$C_6H_4Br{\cdot}COMe$ and *o*-$C_6H_4F{\cdot}COPh$, showing that factors besides the tenacity of halogen to the C_6H_6 nucleus are operative in the conversion of *o*-halogenoacylbenzenes into benz*iso*oxazoles. (I) and MgEtI afford *o*-*fluoropropiophenone*, b.p. 95—99°/19 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 170°). *o*-$C_6H_4Me{\cdot}CN$ and MgMeI yield *o*-$C_6H_4Me{\cdot}COMe$, b.p. 92°/15 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 161°; semicarbazone, m.p. 211° (lit. m.p. 203°)]. *o*-$OMe{\cdot}C_6H_4{\cdot}COMe$, b.p. 122—124°/16 mm. (semicarbazone, m.p. 181°; 2 : 4-*dinitrophenylhydrazone*, m.p. 160°), is obtained similarly. Short boiling of $CH_2Ph{\cdot}CO{\cdot}C_6H_4Br$-*o* with 2 : 4-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ in MeOH containing HCl gives 3-*benzyl*-1-2′ : 4′-*dinitrophenyliso*-*indazole*, m.p. 199—200°. H. W.

***iso*Benzoxazoles. V.**—See A., 1942, II, 56.

Tri-(4-phenylbenzthiazylthiomethylene)amine.—See B., 1941, II, 419.

Benzthiazyl-1-sulphamine.—See B., 1941, II, 446.

VII.—ALKALOIDS.

South African *Senecio* alkaloids, the cause of "dunsiekte" [liver cirrhosis] in animals and bread poisoning in human beings. H. L. de Waal (*J. South Afr. Chem. Inst.*, 1941, **24**, 29—34).—*Retrorsine*, $C_{18}H_{25}O_6N$, m.p. 215—216°, hydrolysed to retronecine (I), $C_8H_{13}O_2N$, and *retronecic acid* (II), $C_{10}H_{16}O_6$, has been isolated from *S. retrorsus*, *S. isatideus*, *S. ilicifolius*, *S. pterophorus*, *S. graminifolius*, and *S. scleratus*; pterophine $C_{12}H_{23}O_5N$, m.p. 227—228°, hydrolysed to (II) and *pterophinecic acid*, from *S. pterophorus* and *S. ilicifolius*; isatidine, hydrolysed with $Ba(OH)_2$ to isatinecic acid, $C_{10}H_{16}O_6$, containing CO_2H and CO_2H, or by KOH–EtOH to *dewalic acid*, $C_{10}H_{16}O_6$, containing 2 CO_2H, and isatinescine containing one pyrrole ring, unlike (I) which contains the pyrrolizidine structure, from *S. isatideus*, *S. retrorsus*, and *S. scleratus*; rosmarinine (III), $C_{18}H_{27}O_6N$, m.p. 209°, hydrolysed to *rosmarinescine* and senecic acid, from *S. rosmarinifolius*; *scleratine*, $C_{18}H_{27}O_7N$, m.p. 180°, from *S. scleratus*; *platyphylline* (IV), $C_{18}H_{27}O_5N$, m.p. 129°, from *S. aduatus*, and senecionine, $C_{18}H_{25}O_5N$, m.p. 235°, from *S. ilicifolius*. All the alkaloids except (III) and (IV) are toxic and cause "dunsiekte." S. C.

Preparation and properties of peimine and peiminine. T. Q. Chou and T. T. Chu (*J. Amer. Chem. Soc.*, 1941, **63**, 2936—2938).—The isolation of peimine (I) and peiminine (II) from *Fritillaria Roylei* is described. Data in the literature (Chou *et al.*, A., 1932, 1178; Chi *et al.*, A., 1936, 1131; 1941, II, 272) are corr. (I) is $C_{26}H_{43}O_2N$, has m.p. 223°, $[\alpha]^{26}_D$ −25° in abs. EtOH, gives a *hydrochloride*, +$3H_2O$ (lost at 120—130°), m.p. indefinite, and anhyd., m.p. 300°, $[\alpha]^{26}_D$ −19° in H_2O, *platini*- and *auri-chloride*, and *diacetate*, m.p. indefinite [*hydrochloride*, +$2H_2O$ (lost at 135—140°), m.p. 293°; *platinichloride*, amorphous]. (II) is obtained from Et_2O having 0·5 H_2O of

crystallisation and then melts at 137°; drying at 110°/vac. gives the anhyd. compound, m.p. 212—213°, $[\alpha]_D^{26}$ −68°; if partly dried at 80°/vac., it resolidifies at 157°. (**II**) gives a *hydrochloride*, $+3H_2O$, m.p. 298°, amorphous *platini-* and auri-*chloride*, *acetate*, m.p. 174° (*hydrochloride*, m.p. 294°), and amorphous *oxime*, decomp. 108° [*hydrochloride*, $+H_2O$ (lost at 135—140°), m.p. indefinite]. R. S. C.

VIII.—ORGANO-METALLIC COMPOUNDS.

Magnetic studies of co-ordination compounds. V. Binuclear copper derivatives of diphenylmethylarsine. D. P. Mellor and D. P. Craig (*J. Proc. Roy. Soc. New South Wales*, 1941, **75**, 27—30; cf. A., 1938, I, 232).—$AsPh_2Me$ (**I**) (1 mol.) and $CuCl_2$ (1 mol.) in EtOH at room temp. for 12 hr. give the brown form of $Cu_2Cl_3(AsPh_2Me)_3$ (**II**); (**I**) added slowly to $CuCl_2,2H_2O$ in EtOH at −50—50° (45 min.), followed by addition of H_2O–EtOH (5 : 2), gives a H_2O-white solution, and in air (24 hr.) the blue form of (**II**) separates. Magnetic measurements show that the mol. of each form contains an unpaired electron. A. T. P.

Lithium *terf.*-butyl. P. D. Bartlett, C. G. Swain, and R. B. Woodward (*J. Amer. Chem. Soc.*, 1941, **63**, 3229—3230).—Li sand (prep. described) with $Bu^{\gamma}Cl$ in presence of a little Mg and $MgBu^{\gamma}Cl$ in Et_2O or C_6H_6 gives $LiBu^{\gamma}$. In Et_2O very fine Li requires only $MgBu^{\gamma}Cl$. The coarser is the Li, the more gas is evolved. Subsequent interaction with CO_2 gives $Bu^{\gamma}CO_2H$ and impure $Bu^{\gamma}CO_2Bu^{\gamma}$. $LiBu^{\gamma}$ causes only reduction of $COBu^{\gamma}_2$, giving $CHBu^{\gamma}_2{\cdot}OH$ (66%), a bimol. reduction product (10%), m.p. 119—121°, and $CH_2{:}CMe_2$. R. S. C.

Effect of metallic halides on the reaction of organo-lithium compounds with alkyl and aryl halides. M. S. Kharasch and W. B. Reynolds (*J. Amer. Chem. Soc.*, 1941, **63**, 3239).—In presence of 2—5 mol.-% of $CoBr_2$, (*a*) LiPh and PhBr give Ph_2 (54%) and homologues, (*b*) LiPh and EtBr give Ph_2, C_3H_8, and C_2H_4, and (*c*) LiBu and PhBu give Ph_2, homologues thereof, C_4H_8, and C_4H_{10}. R. S. C.

Organo-metallic compounds. Electroisomerism in the triethyltin group. T. Harada (*Bull. Chem. Soc. Japan.*, 1941, **16**, 292; cf. A., 1941, II, 284).—The difference in rates of oxidation of two preps. of $SnEt_3$ is attributed to impurity, and not to a difference in their electroisomeric constitutions (cf. *loc. cit.*). A. T. P.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Gramicidin and tyrocidine from *Bacillus brevis*.—See A., 1942, III, 61.

XI.—ANALYSIS.

Determination of concentration of organic and inorganic substances.—See A., 1942, I, 71.

Simplified micro-hydrogenation apparatus. I. B. Johns and E. J. Seiferle (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 841—843).—A simple apparatus for quant. catalytic micro-hydrogenation is described and details of the necessary corrections for temp. and pressure changes are given. An accuracy of ±2% is attained. J. D. R.

Ammonia distillation in the Kjeldahl nitrogen determination. R. Lechner and M. Ross (*Z. Spiritusind.*, 1940, **63**, 243).—Slight neutralisation of acid by the distillate was observed when pure 33% aq. NaOH was distilled with Zn; this was due to splashing of NaOH with the H_2 evolved and was not prevented by the interposition of a trap. The error does not arise when the conc. NaOH has been added to conc. H_2SO_4 (with or without the presence of Se reagent) as in the Kjeldahl determination. I. A. P.

Woburn iodine absorption method. Measurement of total unsaturation in presence of conjugated double bonds. J. D. von Mikusch and C. Frazier (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 782—785).—Standard methods of determination of total unsaturation by various halogen addition methods are exhaustively discussed, and data are presented to show the varying results obtained with different oils, and the dependence of the I val. on concn. of reagent, wt. of sample, etc. Woburn I solution is 0·3(±0·01)N-IBr in AcOH (details of prep. given). In determination of I val. the oil, dissolved in $CHCl_3$, is treated with 500—800% excess of IBr at 20° for 1 hr.; aq. KI is then added and the excess of halogen titrated with $Na_2S_2O_3$. Minor variations of procedure are detailed for use with tung and oiticica oils. The error is ±0·5%. J. D. R.

Determination of hydroxyl content of organic compounds. Acetyl chloride as a reagent. B. E. Christensen, L. Pennington, and P. K. Dimick (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 821—823).—The weighed OH-compound is cooled in solid CO_2, treated with a measured excess of AcCl, allowed to warm to room temp., and after 20 min. the excess of AcCl is decomposed with H_2O and the liberated acid titrated, and the titre compared with a blank test. The method is as accurate as the older methods, and more rapid, but fails in certain cases *e.g.*, salicylic acid, picric acid, and with substances which can add HCl. J. D. R.

Analytical procedures employing [the] Karl Fischer reagent. VII. Alternative method for determination of acid anhydrides. D. M. Smith, W. M. D. Bryant, and J. Mitchell, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 1700—1701; cf. A., 1941, II, 180).—Anhydrides are determined (±0·3%) by heating for 1 hr. at 60±1° with C_5H_5N containing 10% (wt./vol.) of NaI and ~1% of H_2O and determining the residual H_2O by the Karl Fischer reagent, a blank on the C_5H_5N–H_2O being conducted simultaneously. The H_2O content of anhydrides is determined similarly but at 0°. Maleic and camphoric anhydride resists determination owing to a Diels–Alder reaction and steric hindrance, respectively. R. S. C.

Determination of citral by means of the photo-electric colorimeter. J. Bailey and C. K. Beebe (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 834—836).—The sample in EtOH is treated with a solution of m-$C_6H_4(NH_2)_2,2HCl$ and $H_2C_2O_4$ in EtOH, and the yellow colour produced is measured photo-colorimetrically and compared with known standards prepared from pure citral (**I**). When dyes are present in commercial samples, blanks using no m-$C_6H_4(NH_2)_2$ are run and the absorption due to dye is allowed for in the calculation of (**I**) content. J. D. R.

Preparation of a solution of *o*-phthalaldehyde for use as a glycine reagent. W. M. Sandstrom and H. A. Lillevik (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 781).—*o*-Xylene in Ac_2O–H_2SO_4 is oxidised with CrO_3 in AC_2O–AcOH at 0°. The product, isolated with Et_2O, is hydrolysed (H_2SO_4) and steam-distilled, and the distillate used for determination of glycine. J. D. R.

Polarographic wave heights in mixtures of benzylideneacetone and acetophenone.—See A., 1942, I, 24.

Alloxan and the " ninhydrin " test. G. N. Copley (*Analyst*, 1941, **66**, 492—493).—Compounds with α-acylamido-groups give a bluish-violet colour with ninhydrin (**I**). Similar, but less intense, colours are produced by higher concns. of alloxan used in the place of (**I**). S. T. P. B.

Microchemical tests for alkaloids and synthetics. G. L. Keenan (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 830—833).—Microchemical detection of physostigmine (eserine) (**I**) ($AuBr_3$), dilaudid (Na nitroprusside), sulphapyridine, and Na sulphapyridine ($AuCl_3$) is satisfactory. Minor improvements in technique are suggested. For (**I**), $AuCl_3$ + NaBr followed by conc. HCl is a satisfactory alternative to $AuBr_3$. A. A. E.

Determination of some amino-acids in chymotrypsinogen, and its mol. wt. E. Brand and B. Kassel (*J. Gen. Physiol.*, 1941, **25**, 167—176).—A method for the determination of the min. mol. wt. of a protein from the distribution of the S-containing NH_2-acids is described. In the case of chymotrypsinogen, the calc. min. mol. wt., 36,700, is the actual mol. wt. and this agrees with the val. of 36,000 found by determination of osmotic pressure (Kunitz and Northrop, A., 1935, 785). Chymotrypsinogen contains protein-S (1·48), methionine (1·22), cysteine (1·29), cystine (3·3), tyrosine (2·96), and tryptophan (5·51%) and the total protein-S is all accounted for as the three S-amino-acids. Each mol. of the protein contains 17 S, and 3 methionine, 4 cysteine, 10 half-cystine (S·S linkings), 6 tyrosine, and 10 tryptophan residues. No reactive SH groups are present, although it yields cysteine on hydrolysis. This may be due to preformed but unreactive SH groups or to SX groups which yield SH on hydrolysis. J. N. A.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

MARCH, 1942.

I.—ALIPHATIC.

Bromination of *cyclo*hexane, methyl*cyclo*hexane, and *iso*butane. M. S. Kharasch, W. Hered, and F. R. Mayo (*J. Org. Chem.*, 1941, **6**, 818—829).—Mixtures of *cyclo*hexane (I), methyl*cyclo*hexane (II), and $CHMe_3$ (III) with Br are allowed to react at about room temp. in glass stoppered or sealed containers. The progress of the reaction between (I) or (II) and Br is estimated in sealed tubes with an error of ±3% by comparison with standard solutions of Br in CCl_4 and in stoppered tubes by titration with KI and $Na_2S_2O_3$. Reactions in sealed tubes are generally allowed to proceed until the mixtures become colourless, when 100% reaction is assumed. Extent of bromination of (III) is determined by titration when the reaction does not reach completion. In the absence of light and O_2 (I), (II), and (III) react only to the extent of 1% per month. In the dark but in presence of O_2 (I) and (II) react to the extent of ~10% per day; light in absence of O_2 has here about the same effect as O_2 without light. Bromination of (III) is more affected by light but less by O_2. Light and O_2 acting together cause the reaction to proceed several hundred times as fast as either agent alone, their combined effect approximating to the product rather than the sum of their individual effects. The effect of O_2 on the photochemical action varies with the pressure, reaching a max. at ~5 cm. In the absence of O_2 the proportion but not the abs. amount of Br reacting with (I) is greater in the more dil. solution. With (II) both proportion and abs. amount are greater. With (III) and higher [Br] the abs. amount of Br reacting appears to be nearly independent of the initial [Br]. In presence of air with (I) and (II) the time required for complete reaction decreases as the initial [Br] is decreased. Similar effects with (I), (II), and (III) are shown under various pressures of O_2. It is evident that bromination is retarded by high [Br]. Peroxides (Bz_2O_2, lauryl peroxide, or ascaridole) do not cause detectable acceleration in the rate of bromination of (I), (II), or (III); in a few experiments a slight retardation is observed. Org. inhibitors ($NHPh_2$, EtOH, PhSH, *iso*-C_5H_{11}·O·NO) cause retardation of bromination. (I) gives exclusively *cyclo*hexyl bromide. (II) affords ~75% of mono- and 25% of di-bromides. (III) yields 60% of CMe_3Br and 40% of CMe_2Br·CH_2Br. The changes are probably represented: $Br_2 + h\nu \rightarrow 2Br$; $RH + Br^{\cdot} \rightarrow R^{\cdot} + HBr$; $R^{\cdot} + Br_2 \rightarrow RBr + Br^{\cdot}$. H. W.

Effect of organic peroxides in chlorination reactions. M. S. Kharasch and M. G. Berkman (*J. Org. Chem.*, 1941, **6**, 810—817).—In an air-free system at 10^{-5} mm. a measured vol. of Cl_2 is condensed by aid of liquid N_2 into a bomb tube containing the hydrocarbon (I) to be chlorinated. The tube is sealed and kept at 0° in the dark for the chosen time. Usually 0·05 mol. of (I) and 0·005 mol. of Cl_2 are used although considerable variations in the relative concns. do not significantly affect the results. HCl and unchanged Cl_2 are determined in the products. Chlorination of *cyclo*hexane, *n*-C_7H_{16}, Bu^tCl, and *cyclo*hexyl chloride proceeds slowly at 0° in the absence of light and catalysts. Org. peroxides markedly accelerate substitution in the dark. Light has a highly accelerating effect. O_2 completely inhibits chlorination. Aromatic hydrocarbons are more readily chlorinated than aliphatic or alicyclic hydrocarbons. Absorption of Cl_2 is relatively rapid in the dark at 0°; hence the effects of light and of peroxides are less marked. O_2 inhibits reaction only slightly. Under the conditions described chlorination occurs both by addition to the aromatic nucleus and by substitution. The % of additive product formed is for C_6H_6 100%, for PhCl >95%, for PhMe 45%, and for $PhBu^{\gamma}$ 35%. At −50° Cl_2 adds to *m*-xylene but at 0° the additive product loses HCl giving substituted *m*-xylenes with 2 Cl in the aromatic nucleus. H. W.

Hexamethylethane and related compounds. F. C. Whitmore, R. E. Marker, and L. Plambeck, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 1626—1630).—Bu^{γ}_2 and its derivatives undergo numerous reactions without rearrangement. Bu^{γ}_2 (purification described), m.p. 101—102° (sealed tube), b.p. 105—106°/732—749 mm., and Cl_2–CCl_4 at 0—10° (sunlight) give *ββγγ-tetramethyl-*n*-butyl chloride* (I) (33%), m.p. 52—53°, b.p. 80—81°/40 mm., and a dichloride (14·5%). With Mg and a trace of I and EtBr in Et_2O, (I) gives a MgCl derivative, which with H_2O regenerates Bu^{γ}_2, with CO_2 gives *ββγγ-tetramethyl-*n*-valeric acid* (II) (59%), m.p. 66—67°, with $HgCl_2$ gives CMe_2Bu^{γ}·CH_2·HgCl (III) (35%), m.p. 170—171°, and with O_2 gives *ββγγ-tetramethyl-*n*-butan-α-ol* (IV) (53%), m.p. 149—150° (*phenylurethane*, m.p. 65—66°; 3 : 5-*dinitrobenzoate*, m.p. 88—89°; *acetate*, b.p. 191—192°/739 mm.), and *ββγγζζηη-octamethyl-*n*-octane* (V) (24%), m.p. 70·0—74·5°. With $SOCl_2$ in C_6H_6, (II) gives the *acid chloride*, b.p. 87—88°/20 mm., and thence the *anilide*, m.p. 175—176°, and the *amide*, dimorphic, m.p. 149—150° and 137—138°, which with aq. NaOBr etc. gives, without rearrangement, *ββγγ-tetramethyl-*n*-butylamine hydrochloride* (VI), sublimes at ~330°, and *NN′-di-ββγγ-tetramethyl-*n*-valerylcarbamide* (VII), m.p. 217—218°. With KCNO at 100°, (VI) gives *ββγγ-tetramethyl-*n*-butylcarbamide*, m.p. 176—177°, also obtained with (II) from (VII) by boiling 50% H_2SO_4. $KMnO_4$–NaOH oxidises (IV) to *ααββ-tetramethyl-*n*-butyric acid*, m.p. 196—197°, which by way of the chloride ($SOCl_2$) yields the *amide*, m.p. 201—202°. P_2O_5 then gives CMe_2Bu^{γ}·CN, m.p. 131—132° (odour of camphor), reduced by Na–EtOH etc. to (VI). I–KI converts (III) in Et_2O into *ββγγ-tetramethyl-*n*-butyl iodide*, b.p. 112—113°/40 mm., which with Mg gives only (V), with Zn–AcOH gives Bu^{γ}_2, and with KOH–EtOH–N_2 at 160—180° gives Bu^{γ}_2 (84%), H_2, and KOAc (83%). Br–NaBr and (III) give *ββγγ-tetramethyl-*n*-butyl bromide*, b.p. 92—93°/40 mm., also reduced to Bu^{γ}_2. R. S. C.

Conversion of acetone into isoprene. H. S. Taylor and W. J. Shenk (*J. Amer. Chem. Soc.*, 1941, **63**, 2756—2757).—OH·CMe_2·C:CH (prep. from $COMe_2$ and C_2Na_2 in 85% yield; cf. Hennion *et al.*, A., 1940, II, 187) with (*a*) Cu–Zn dust in H_2O gives 50—55% or with (*b*) H_2–Pd in aq. polyvinyl alcohol gives 84% of OH·CMe_2·CH:CH_2, which over activated Al_2O_3 at 290—300° gives isoprene [88% or >70% overall when methods (*a*) and (*b*), respectively, are used]. R. S. C.

Manufacture of alkyl halides.—See B., 1941, II, 411.

Preparation of ethyl chloride.—See B., 1941, II, 411.

Oxygen effect in the reaction of bromine with neopentane, *tert.*-butylbenzene, and trimethylacetic acid. M. S. Kharasch and M. Z. Fineman (*J. Amer. Chem. Soc.*, 1941, **63**, 2776—2779).—In absence of O_2, Br does not react with CMe_4, but does so when illuminated in presence of O_2 at 80° or of org. peroxides at 50°. Illumination of $PhBu^{\gamma}$–Br–O_2 at 80° gives only nuclear Br-compounds. $Bu^{\gamma}CO_2H$ reacts only at 150°, giving HBr, CO_2, brominated hydrocarbons, and 9% of $Bu^{\gamma}CO_2$·CH_2·CMe_2·CO_2H, but no CO. R. S. C.

Peroxide effect in the addition of halogen acids to olefines. XXVI. Addition of halogen acids to trichloromethylethylene. M. S. Kharasch, E. H. Rossin, and E. K. Fields (*J. Amer. Chem. Soc.*, 1941, **63**, 2558—2560; cf. A., 1940, II, 362).—CCl_3·CHMe·OH (prep. from chloral, MgMeBr, and $MnCl_2$), m.p. 46—49°, b.p. 63—65°/20 mm., and P_2O_5 give

CH_2:CH·CCl_3 (**I**), b.p. 57°/103 mm. (cf. Henry, A., 1905, i, 558; Vitoria, *ibid.*, 110), and (?) *aa-dichloroallene*, b.p. 52—53°/103 mm. HCl does not add to (**I**) at room temp.; in presence of $FeCl_3$ (3 mols.) at room temp. interaction is slow but at 50° 20% of CCl_3·CHMeCl is formed in 50—100 hr. Addition of HBr is difficult, but in presence of Bz_2O_2 *aaa-trichloro-γ-bromopropane*, b.p. 115—116°/103 mm., 184—186°/751 mm., lachrymatory, is obtained. These results do not agree with the views of Robinson (Smith, A., 1938, II, 258). R. S. C.

Joint action of tetralin hydroperoxide and nitro-compounds on the polymerisation of chloroprene.—See A., 1942, I, 106.

Substituted acetylenes and their derivatives. XLIII. Reduction of multiple carbon–carbon linkings. III. Preparation of olefines from acetylenes. K. N. Campbell and L. T. Eby (*J. Amer. Chem. Soc.*, 1941, **63**, 2683—2685; cf. A., 1941, II, 81).—Reduction of the acetylene by Na in liquid NH_3 gives Δ^{α}-hexene, f.p. −141°, b.p. 63·15°/750 mm., -heptene, f.p. −120°, b.p. 92·8°/749 mm., and -octene, f.p. −102°, b.p. 120·75°/742 mm., *trans*-Δ^{β}-hexene, f.p. −133·5°, b.p. 67·55°/750 mm., *trans*-Δ^{β}-, f.p. −88°, b.p. 123·35°/750 mm., -Δ^{γ}-, f.p. −108°, b.p. 122·4°/741 mm., and -Δ^{δ}-octene, f.p. −94°, b.p. 121·4°/739 mm., *trans*-Δ^{ϵ}-decene, f.p. −73°, b.p. 170·2°/739 mm., β-methyl-Δ^{γ}-buten-β-ol, f.p. −43°, b.p. 96·1—97·1°/744 mm., and *trans*-β-methyl-Δ^{γ}-octen-β-ol, b.p. 177·1—178·4°/751 mm. Hydrogenation (Raney Ni) of the acetylenes gives slightly less pure Δ^{α}-olefines and *cis*-Δ^{β}-, f.p. −146°, b.p. 68·25°/749 mm., and -Δ^{γ}-hexene, f.p. −133°, b.p. 66·8—66·9°/741 mm., *cis*-Δ^{β}-, f.p. −104°, b.p. 124·6°/750 mm., -Δ^{γ}-, f.p. −126°, b.p. 122·3°/741 mm., and -Δ^{δ}-octene, f.p. −118°, b.p. 121·7°/739 mm., *cis*-Δ^{ϵ}-decene, f.p. −112°, b.p. 169·5—169·6°/739 mm., and *cis*-β-methyl-Δ^{γ}-octen-β-ol, b.p. 176·5—176·8°/743 mm. The following are also recorded: Δ^{α}-, f.p. −132°, b.p. 71·2°/751 mm., Δ^{β}-, f.p. −88°, b.p. 83·85°/742 mm., and Δ^{γ}-hexinene, f.p. −101°, b.p. 81·2—81·3°/747 mm.; Δ^{α}-, f.p. −79°, b.p. 125·2°/737 mm., Δ^{β}-, f.p. −62°, b.p. 137·1°/742 mm., Δ^{γ}-, f.p. −105°, b.p. 132·8—132·9°/747 mm., and Δ^{δ}-octinene, f.p. −102°, b.p. 131·8—132·1°/747 mm.; Δ^{ϵ}-decinene, f.p. −73°, b.p. 177·15°/751 mm.; *n*-hexane, f.p. −94°, b.p. 68·6°/747 mm., -heptane, f.p. −90°, b.p. 97·6°/747 mm., -octane, f.p. −57°, b.p. 125·1°/747 mm., and -decane, f.p. −30°, b.p. 173·4°/747 mm.; β-methyl-Δ^{γ}-butinen-β-ol, f.p. 2°, b.p. 103·2—103·4°/749 mm.; β-methyl-Δ^{γ}-octinen-β-ol, f.p. −44°, b.p. 181·5—181·6°/743 mm. *d* and *n* (four λ) are recorded. The Δ^{α}-isomerides have the lowest b.p., *n*, and *d*, and the Δ^{β}- have the highest vals., which then decrease as the C:C is moved towards the centre of the chain. Structure and f.p. are not generally related, except that the f.p. of the *cis*- is lower than that of the *trans*-olefine. R. S. C.

Oxidation. II. Oxidation of di*iso*butylene in presence of potassium hydroxide at elevated temperature and pressure. R. W. Bost and L. B. Lockhart, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 2790—2792).—Oxidation of di*iso*butylene (1 mol.) in presence of solid KOH at 100°/125 lb. is complete in 8 hr. (including an induction period of 1·5—2 hr.) with consumption of 2·00 O_2 and gives $COMe_2$ 0·055, COMe·CH_2Bu^{γ} 0·070, other CO-compounds 0·161, HCO_2H 0·31, $Bu^{\gamma}CO_2H$ 0·077, CO_2 0·20 mol., and some residual gum. R. S. C.

Chlorinated derivatives of *iso*propyl fluoride. A. L. Henne and F. W. Haeckl (*J. Amer. Chem. Soc.*, 1941, **63**, 2692—2694).—Chlorination of C_3H_8 is random; that of $CMeCl_2$·CH_2Cl gives $CMeCl_2$·$CHCl_2$ (2 parts) and $CCl_2(CH_2Cl)_2$ (1 part); $CMeCl_2$·CCl_3 resists further chlorination; that of CMe_2ClF is as directed as that of CMe_2F_2 or $CEtF_3$. CH_2:CCl·CH_2Cl [prep. from $CHCl(CH_2Cl)_2$ by boiling 40% NaOH–EtOH or 30% aq. NaOH], b.p. 92·5°, and HF at 50—60° (later room temp.) give *aβ-dichloro-β-fluoropropane* (**I**), f.p. −92·5° to −92·7°, b.p. 88·5°, and a little $CMeF_2$·CH_2Cl, f.p. −56·2°, b.p. 55—55·2°. With Cl_2, (**I**) gives successively (*a*) *aaβ-trichloro-β-fluoropropane*, solidifies to a glass, b.p. 116·7°, and a trace of $CClF(CH_2Cl)_2$, (*b*) *aaaβ-*, f.p. 104—104·5°, b.p. 139·6°, and a little *aaβγ-tetrachloro-β-fluoropropane*, solidifies to a glass, b.p. 50—51°/14 mm., and (*c*) slowly and only in sunlight *aaaβγ-penta-*, f.p. −34·4°, b.p. 72°/14 mm., *aaaβγγ-hexa-*, f.p. −31·6° to −33·5°, b.p. 87°/14 mm., and *aaaβγγγ-hepta-chloro-β-fluoropropane*, f.p. 7·6—8·4°, b.p. 105°/14 mm. *n* and *d* are recorded for the products. Structures, in so far as they are in question, are deduced from the b.p. and stability. R. S. C.

Mechanism of the catalytic dehydration and dehydrogenation of alcohols of the homologous series C_nH_{2n+1}·OH.—See A., 1942, I, 107.

Preparation of ethinylcarbinols.—See B., 1941, II, 411.

Conversion of the γ-chlorobutan-β-ols into the βγ-dichlorobutanes; evidence for a cyclic intermediate. H. J. Lucas and C. W. Gould, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 2541—2551). —*cis*-, m.p. 34·45—34·55°, and *trans*-(:CHMe)$_2$, m.p. 41·9—42·1°, with Cl_2, best at −20° in diffused artificial light, give *dl*-, b.p. 53·16°/80 mm., 117·10°/760 mm., and *meso*-(CHMeCl)$_2$, b.p. 49·52°/80 mm., 113·14°/746 mm., respectively. *trans*-βγ-Epoxybutane with conc. HCl at 5° gives *dl-erythro*-γ-chlorobutan-β-ol (**I**), b.p. 56·1°/30 mm., 135·4°/748 mm. *dl-threo*-γ-Chlorobutan-β-ol (**II**), b.p. 52·0°/30 mm., 130·8°/748 mm., is obtained similarly from *cis*-βγ-epoxybutane, from *cis*-(:CHMe)$_2$ by $Bu^{\gamma}OCl$ (not NHAcCl) and a little H_2SO_4 in H_2O–AcOH at 0°, or, with some of its acetate, b.p. 70—72·5°/30 mm., from *meso*-(CHMe·OAc)$_2$ and conc. HCl with a trace of H_2SO_4 at 50—60°. Resolution of (**I**) by brucine in Ac_2O–$CHCl_3$ at 50° gives (**I**) having [α] +0·82° (in this and other cases $[\alpha]_D^{25}$) and its acetate, [α] −3·37°. Brucine and (**II**) in ligroin give (**II**) having [α] up to +1·10°. With PCl_5–$CHCl_3$, (**I**) gives a mixture, with boiling $SOCl_2$ gives, by way of a chlorosulphite, *meso*-(CHMeCl)$_2$ [16%; also obtained from (+)-(**I**)], and with PCl_3 (20% yield) or $SOCl_2$–C_5H_5N (63% yield) gives *dl*-(CHMeCl)$_2$. (+)-(**I**), [α] +0·82°, with $SOCl_2$–C_5H_5N gives (CHMeCl)$_2$ having [α] −3·80°. With $SOCl_2$–C_5H_5N, (**II**) gives *meso*- + (+)-, and with $SOCl_2$ gives *dl*-(CHMeCl)$_2$ with the *sulphite*, b.p. 85—87°/0·1—0·2 mm., [α] −11·29°, of (**II**). (−)-(CHMeCl)$_2$ is only slowly racemised in $SOCl_2$ at 100°. (**I**) and (**II**) are unaffected by 46% HCl at room temp., HCl–$ZnCl_2$ at 100°, or 60% HBr at 100°. The purity of *dl*- and *meso*-(CHMeCl)$_2$ is best measured by dipole moments. The reaction of (**I**) or (**II**) with $SOCl_2$ is interpreted as proceeding by way of a cyclic dimethylethylene chloronium ion. Mechanisms, inversions, and structures are discussed in detail. R. S. C.

Action of magnesium *tert.*-butyl chloride on propylene oxide. P. G. Stevens and J. A. McCoubrey (*J. Amer. Chem. Soc.*, 1941, **63**, 2847—2848).—Propylene oxide and $MgBu^{\gamma}Cl$, best at 25° (7 weeks), give CH_2Bu^{γ}·CHMe·OH (11%) (3 : 5-dinitrobenzoate, m.p. 92·5—93°; *α-naphthylurethane*, m.p. 107—108°). CH_2:$CMeBu^{\gamma}$ and HBr–ascaridole at −78° give $CHMeBu^{\gamma}$·CH_2Br, the Mg derivative from which with O_2 gives *βγγ-trimethyl*-n-*butan-α-ol*, b.p. 159·5—162°/761 mm. R. S. C.

Manufacture of glycerol from starch.—See B., 1941, II, 409.

Chlorination of ethylenic compounds containing a reactive group by *tert.*-butyl hypochlorite in methanol. B. L. Emling, R. R. Vogt, and G. F. Hennion (*J. Amer. Chem. Soc.*, 1941, **63**, 1624—1625).—Allyl chloride and $Bu^{\gamma}OCl$ (1 mol.) with a little *p*-$C_6H_4Me·SO_3H$ in MeOH (4 mols.) at 40° give OMe·$CH(CH_2Cl)_2$ (**I**) (44%). Similarly, CH_2:CMe·CH_2Cl gives *aγ-dichloro-β-methoxy*isobutane (35%), b.p. 170°/748 mm., and CHPh:CH·CO_2H gives OMe·CHPh·CHCl·CO_2Me (24%), m.p. 53—54°, and the corresponding acid (**II**) (1%), m.p. 161—162°. With $Bu^{\gamma}OCl$ (2 mols.) in MeOH (4 mols.), CHPh:CH·CHO gives *α-chloro-β-methoxy-β-phenylpropaldehyde*, b.p. 114°/5 mm. [oxidised by $K_2Cr_2O_7$–H_2SO_4 to (**II**)]. With $Bu^{\gamma}OCl$ (1 mol.) in MeOH (2 mols.) CH_2:CH·CH_2·OH gives *γ-chloro-β-methoxypropyl* (20%), b.p. 68—69°/5 mm. [converted by PCl_5 into (**I**)], *γ-chloro-β-allyloxypropyl* (**III**) (7%; 36% obtained in absence of MeOH), b.p. 91—92°/10 mm., and *γ-chloro-β-γ'-chloro-β'-methoxy*-n-*propoxy*-n-*propyl alcohol* (2%), b.p. 123°/5 mm. [obtained in 50% yield from (**III**) and $Bu^{\gamma}OCl$–MeOH]. R. S. C.

Thermal decomposition of methyl *n*-butyl ether.—See A., 1942, I, 102.

Di-*tert.*-butyl ether. J. L. E. Erickson and W. H. Ashton (*J. Amer. Chem. Soc.*, 1941, **63**, 1769).—$Bu^{\gamma}Cl$ and Ag_2O in Et_2O give *di*-tert.-*butyl ether* (**I**) (35%), b.p. 106·5—107°, $Bu^{\gamma}OH$, CH_2:CMe_2, CO_2, and AgCl. With conc. HCl, (**I**) gives exothermally $Bu^{\gamma}Cl$ (1·9 mols.). Models are inadequate for predicting existence of ethers such as (**I**). R. S. C.

Properties of chloromethanesulphonyl chloride. Chloromethanesulphonamides. T. B. Johnson and I. B. Douglass (*J. Amer. Chem. Soc.*, 1941, **63**, 1571—1572).—$CH_2Cl·SO_2Cl$ (**I**), b.p. 77°/23 mm., gives *chloromethanesulphon-amide* (**II**), m.p. 73—74°/b.p. 185°/20 mm., *-anilide* (**III**), m.p. 81—82°,

-p-*toluidide*, m.p. 96—97°, and -*diethylamide* (**IV**), m.p. 45°. The Cl of (**II**) or (**III**) does not react with NH_2Ph at the b.p. or 100°. In boiling 5% NaOH, (**II**) gives readily CH_2O, NH_3, NaCl, and Na_2SO_3. Hydrolysis of (**I**) by H_2O gives $CH_2Cl{\cdot}SO_3H$ (**V**), which is stable (10 min.) to 5% NaOH. Thus decomp. of (**II**) by OH^- is primarily to $CH_2Cl{\cdot}OH$ and $^-SO_2{\cdot}NH_2$. Loss of Cl in boiling 5% NaOH is 100 and 63% in 10 min. for (**II**) and (**III**), respectively, and 3% in 30 min. for (**IV**); in boiling 5% NaOH–EtOH it is 43 and 20% in 1 hr. for (**IV**) and (**V**), respectively. Hydrolysis is probably by fission of the C·S linking in all cases, its ease depending on the presence of enolisable H on the N. R. S. C.

Preparation of trichloromethanesulphonyl chloride. M. S. Schechter and H. L. Haller (*J. Amer. Chem. Soc.*, 1941, **63**, 1764—1765).—$CCl_3{\cdot}SCl$, b.p. 65—68°/50 mm., is best obtained from CS_2 and Cl_2 in presence of a little I at >30°/slightly >1 atm. and is best (50%; 30—35 min.) converted into $CCl_3{\cdot}SO_2Cl$, m.p. 140—140·5° (corr.), by conc. HNO_3 in boiling AcOH. R. S. C.

Sulphonation of *iso*butylene. II. β-Methyl-Δβ-propene-α-sulphonic acid and related compounds. C. M. Suter, J. D. Malkemus, and S. Archer (*J. Amer. Chem. Soc.*, 1941, **63**, 1594—1597; cf. A., 1941, II, 183).—$CH_2{:}CMe_2$ with dioxan–SO_3 in $(CH_2Cl)_2$ at 0° gives di*iso*butylenedisulphonic acid (*Ba* salt) and β-methyl-Δβ-propene-α-sulphonic acid [*Na* (**I**) and *benzylthiuronium* salt (**II**), m.p. 155·8—156·6° (corr.)] with some β-hydroxy*iso*butane-α-sulphonic acid (**III**) and polymerides. With $ClSO_3H$–dioxan in $(CH_2Cl)_2$ it gives Bu^tCl, di*iso*butylene, di*iso*butylenesulphonic acid, and (**I**). The amounts of the products vary according to the conditions. The amount of polymerisation is less with rapid reaction. $ClSO_3H$ at −70° gives only polymerides. $CMe_2{:}CHCl$ does not react with aq. Na_2SO_3. Addition of $POCl_3$ to $CH_2{:}CMe{\cdot}CH_2Cl + Na_2SO_3$ gives *β-methyl-Δβ-propene-α-sulphonyl chloride* (**IV**), b.p. 68—70°/8 mm., also obtained from (**I**) by $POCl_3$ and converted by $NHPh{\cdot}CH_2Ph$–C_6H_6 into the *benzylanilide*, m.p. 78·5—79·5°. *iso*Butylene oxide and aq. $NaHSO_3$ give the *Na* salt of (**III**), converted by $POCl_3$ at 100° into (**IV**) and thence into (**II**). H_2S is the sole product recognised when (**IV**) is reduced by Zn in aq. H_2SO_4 at −5°. With PBr_3–Br at 0° and later 85°, (**I**) gives $CMeBr(CH_2Br)_2$, also obtained (b.p. 75·5°/5 mm.) from $CH_2{:}CMe_2$ and converted by KOAc–AcOH into $CHBr{:}CH{\cdot}CH_2{\cdot}OAc$, b.p. 84—85°/13 mm. Sulphonation may proceed by way of $CMe_2{:}C\langle^{CH_2\cdot SO_2}_{O-SO_2}\rangle O$. R. S. C.

Manufacture of acetic anhydride.—See B., 1941, II, 412.

Ammonium salts of aliphatic carboxylic acids.—See A., 1942, I, 111.

Electrolytic reduction of sorbic acid. Factors influencing the formation of bimolecular products. C. L. Wilson and K. B. Wilson (*Trans. Electrochem. Soc.*, 1941, **80**, *Preprint* 29, 365—376; cf. A., 1939, II, 241).—The formation of bimol. reduction products (**I**) by the electrolytic reduction of sorbic acid (**II**) is highest at Hg and Pb cathodes and is very low at Tl and spongy Cu cathodes. It is higher in acid than in alkaline solution. In alkaline solution and at a Hg electrode it increases with increasing c.d. and with decreasing temp., *i.e.*, with conditions leading to a high H_2-overvoltage. The results are consistent with the view that the formation of (**I**) occurs through the capture of single electrons and protons by adsorbed (**II**) mols. and subsequent union of the radicals so formed, the increase in cathode potential probably enhancing the adsorption of depolariser on the cathode. J. W. S.

Electrolytic reduction of organic compounds. IV. Bimol. products from sorbic acid at a solid and liquid gallium cathode: analogy with overvoltage. K. B. Wilson and C. L. Wilson (*J.C.S.*, 1941, 874—877; cf. preceding abstract).—Reduction of sorbic acid at solid and liquid Ga or Wood's metal cathodes in 0·5N-$NaHCO_3$ or 2N-KOH gives a mixture of H_2-acids and a bimol. product. There is an increase in the formation of the latter at the m.p. of Ga. A. Lr.

Absorption of oxygen in the enzymic oxidation of unsaturated fatty acids. H. Süllmann (*Helv. Chim. Acta*, 1941, **24**, 1360—1380).—"Lipoxidase" (**I**), obtained from the aq. extract of the de-fatted soya bean, has only a slight catalytic influence on the addition of O_2 to singly unsaturated fatty acids (oleic and recinoleic acid); these acids have relatively low activity in the secondary oxidation of carotene. Polyunsaturated fatty acids absorb considerable amounts of O_2 in presence of (**I**). When the I vals. of the preps. are taken into account it appears that the enzymic oxidation of the doubly unsaturated linoleic acid causes mainly absorption of 1 mol. of O_2 and of the trebly unsaturated linolenic acid causes absorption of 2 mols. of O_2 per mol. of acid. The consumption of O_2 caused by (**I**) is not substantially increased in presence of carotene. O_2 absorption is very rapid at first but the rate diminishes after 5—30 min. In certain experiments there is evidence of the development of autocatalytic processes, probably chain reactions. (**I**) is thermolabile. Protracted dialysis (65 hr.) of (**I**) solution diminishes its activity by about one third. NaCN, in concn. up to 0·025M. in the experimental solution, diminishes the activity of (**I**) by almost one third. H. W.

Homologous series of α-substituted aliphatic acids. P. A. Levene and M. Kuna (*J. Biol. Chem.*, 1941, **141**, 391—406; cf. A., 1936, 1484).—The establishment of max. rotations of homologous series of α-OH-, -Br-, and $-NH_2$-acids is studied. *d*(−)-α-OH·CHEt·CO_2H, through the morphine salt, gives a *Ba* salt, $[M]_D^{25}$ +14·9° in H_2O (max. rotation), and *d*(+)-OH·$CHBu^a{\cdot}CO_2H$ affords, through the cinchonidine salt, a *Ba* salt, max. $[M]_D^{25}$ +22·2° in H_2O. (−)-α-$CHMeBr{\cdot}CO_2H$ has max. $[M]_D^{25}$ −57° in Et_2O [Me ester, max. $[M]_D^{25}$ −84° (homogeneous)]. *dl*-$CHEtBr{\cdot}CO_2H$ and brucine in $COMe_2$–$CHCl_3$ yield brucine salts, and thence (+)-$CHEtBr{\cdot}CO_2H$ (**I**), b.p. 66—69°/0·04 mm., max. $[M]_D^{25}$ +66° in Et_2O (12% racemisation after 1 year) [Me ester, b.p. 57—59°/11 mm., max. $[\alpha]_D^{25}$ +93° (homogeneous)]. (−)-$CHEtBr{\cdot}CO_2H$ has $[M]_D^{25}$ −57·4° in Et_2O (87% of max.). Resolution through the strychnine salt gives (−)-$CHBu^aBr{\cdot}CO_2H$, b.p. 90—92°/1 mm., $[M]_D^{25}$ −82° in Et_2O (1·4% racemisation on distillation) [Me ester, b.p. 60—61°/1 mm., max. $[M]_D^{25}$ −104° (homogeneous)]. (**I**), $[\alpha]_D^{25}$ +26·5° (homogeneous), and aq. NH_3 at room temp. (2 days) give *l*(+)-α-*amino*-n-*butyric acid* (**II**), max. $[M]_D^{25}$ +21·1° in 20% HCl; similarly prepared is *d*(−)-α-amino-*n*-hexoic acid, $[M]_D^{25}$ −28° in 20% HCl. *l*(+)-Alanine (**III**), $[\alpha]_D^{29}$ +7·1° in 20% HCl (46% of max. val.), and aq. $NaNO_2$–H_2SO_4 at 28° or 0°, or $NaNO_2$–AcOH at 90°, followed by esterification, give $OH{\cdot}CHMe{\cdot}CO_2Et$, $[\alpha]_D^{20}$ −4·06° (homogeneous) (28% of max. val.; 39% racemisation), −5·05° (35% of max.; 24% racemisation), or −3·79° (43% racemisation), respectively. (**III**), $[\alpha]_D^{25}$ +14·7° in 20% HCl (96% of max.), and NOBr–Et_2O at room temp. yield a bromopropionic acid having $[M]_D^{25}$ −31·4° (homogeneous) (25·6% racemisation). *dl*-$(OH{\cdot}CHEt{\cdot}CO_2)_2Ba$ and aq. HBr–Br–NO at 0° give a Br-free acid, b.p. 138—144°/15 mm. (**II**), $[\alpha]_D^{25}$ +10° in 20% HCl, affords *l*-OH·CHEt·CO_2Et, $[M]_D^{25}$ −12·8° (15% racemisation), and *l*(+)-$NH_2{\cdot}CH_2Et{\cdot}CO_2H$, $[\alpha]_D^{25}$ +17·3° in 20% HCl, gives a OH-acid [*Ba* salt, $[M]_D^{25}$ −14·9° (15% racemisation)]. (**II**), $[\alpha]_D^{25}$ +7·5° in 20% HCl, and NOBr give $CHEtBr{\cdot}CO_2H$, b.p. 103—108°/15 mm. (13·5% racemisation). *d*(−)-$NH_2{\cdot}CHBu^a{\cdot}CO_2H$, $[\alpha]_D^{25}$ −21·4° in 20% HCl (88% of max. val.), give the OH-acid (*Ba* salt, $[M]_D^{24}$ +14·4° in H_2O; 25% racemisation) and also (NOBr) (+)-$CHBu^aBr{\cdot}CO_2H$, b.p. 86—89°/0·35 mm. (22% racemisation). *d*(+)-$(OH{\cdot}CHBu^a{\cdot}CO_2)_2Ba$ has $[\alpha]_D^{25}$ +7·31° in H_2O (66% of max. val.) (Et ester, b.p. 49—53°/0·6 mm.). A. T. P.

Phenacyl, *p*-phenyl- and *p*-bromo-phenacyl, and *p*-nitrobenzyl esters of α-hydroxy-fatty acids. D. Price and R. Griffith (*J. Amer. Chem. Soc.*, 1941, **63**, 1767—1768).—The following are prepared. *Phenacyl*, m.p. 55·5—56·5°, p-*phenyl*-, m.p. 88·0—89·7°, and p-*bromo-phenacyl*, m.p. 95·0—95·8°, and *p*-nitrobenzyl, an oil, α-*hydroxy*-n-*octoate*. *Phenacyl*, m.p. 60·0—60·5°, p-*phenyl*-, m.p. 80·3—80·8°, and p-*bromophenacyl*, m.p. 93·0—93·5°, and p-*nitrobenzyl*, m.p. 54·5—55·5°, α-*hydroxy*-n-*decoate*. *Phenacyl*, m.p. 63·5—64·0°, p-*bromophenacyl*, m.p. 91·0—91·5°, and p-*nitrobenzyl*, m.p. 59·0—59·5°, α-*hydroxy*-n-*dodecoate*. *Phenacyl*, m.p. 69·0—69·5°, p-*bromophenacyl*, m.p. 95·0—95·4°, and p-*nitrobenzyl*, m.p. 67·0—67·8°, α-*hydroxy*-n-*tetradecoate*. *Phenacyl*, m.p. 69·8—70·1°, p-*bromophenacyl*, m.p. 96·0—96·5°, and p-*nitrobenzyl*, m.p. 69·5—70·5°, α-*hydroxypalmitate*. *Phenacyl*, m.p. 76·4—76·8°, p-*bromophenacyl*, m.p. 98·0—98·5°, and p-*nitrobenzyl*, m.p. 76·5—77·0°, α-*hydroxystearate*. The *p*-phenylphenacyl esters of the C_{12}-, C_{14}-, C_{16}-, and C_{18}-acids could not be purified. M.p. are corr. R. S. C.

Production of glycollic and derivatives.—See B., 1941, II, 412.

Purification of lactic acid.—See B., 1941, II, 412.

Photolysis of simple alkyl esters.—See A., 1942, I, 108.

Manufacture of *iso*propyl esters of aliphatic acids.—See B., 1941, II, 413.

Thermal and photochemical decomposition of oxalyl bromide.—See A., 1942, I, 109.

Manufacture of polycarboxylic acids.—See B., 1941, II, 413.

Oxidation of pinene to maleic anhydride.—See B., 1941, II, 409.

Reduction of tartaric acid. H. J. Lucas and W. Baumgarten (*J. Amer. Chem. Soc.*, 1941, **63**, 1653—1657).—Attempts to reduce Bu^{β}_2 tartrate, a solid, b.p. 155—160°/5 mm., Et_2 or Bu^{β}_2 *iso*propylidenetartrate (prep. described), b.p. 125°/2 mm., failed. $(OBz{\cdot}CH{\cdot}CO_2H)_2$, m.p. 193° (lit. 173°), with $SOCl_2$, $SOCl_2$–$ZnCl_2$, or PCl_5 gives the anhydride, whence the alkyl H esters are obtained as undistillable oils. $(OH{\cdot}CH{\cdot}CO_2H)_2$ and 3% HCl–Ac_2O at 60° give diacetyltartaric anhydride (95%), m.p. 134°, converted by MeOH into Me H diacetyltartrate (75%), m.p. 124·7° (corr.) (lit. 102°), $[\alpha]_D^{25}$ −18·4° in MeOH, which with $SOCl_2$ at 60° gives l-threo-*γ-carbomethoxy-αβ-diacetoxy*-n-*butyryl chloride* (**I**), m.p. 108·5° (corr.). The corresponding *Et*, b.p. 137·5°/6 mm., Bu^{β}, b.p. 147°/6·5 mm., and Pr^{β} esters are similarly prepared. Hydrogenation (Pd–$BaSO_4$) of (**I**) in xylene at 130—135° gives *Me* l-*diacetylthreuronate* (65—70%), m.p. 84°, $[\alpha]_D^{25}$ −34·4° in H_2O, −55·2° in MeOH, −35·4° in HCl–MeOH [p-, m.p. 143° (corr.), and 2 : 4-*di-nitrophenylhydrazone*, m.p. 148° (corr.)]. This is unstable in MeOH and still more so in HCl–MeOH ([α] becomes +22°), is completely hydrolysed in H_2O, is unaffected by $Al(OPr^{\beta})_3$ or catalytic hydrogenation, but is reduced by Na–Hg–H_2O at 0—25° to *l*-threonic acid, a syrup [brucine salt, m.p. 203—204° (decomp.), $[\alpha]_D^{25}$ −23° in H_2O]. In acid this gives the lactone and it is reduced by Na–Hg–H_2SO_4 at 0° to *l*-threitol, m.p. 88°, $[\alpha]_D^{25}$ −4·2° in H_2O [$(CHPh)_2$ derivative, m.p. 221—223° (corr.), $[\alpha]_D^{25}$ +79° in $CHCl_3$]. R. S. C.

Oxidation of alcohols to aldehydes.—See B., 1941, II, 413.

Pyrolysis of formaldoxime.—See A., 1942, I, 105.

Production of aldehydes, ketones and other oxygen-containing compounds.—See B., 1941, II, 413.

Structure of the bisulphite compound of acetaldehyde. R. L. Shriner and A. H. Land (*J. Org. Chem.*, 1941, **6**, 888—894).—The presence of a C–S linking in the MeCHO–$KHSO_3$ compound has been established. Freshly distilled MeCHO is transformed by H_2S and 6M-HCl into $(MeCHS)_3$, which when suspended in H_2O at 0° and treated with Cl_2 affords $CHMeCl{\cdot}SO_2Cl$ (**I**), b.p. 48—53°/3 mm., also obtained from $CHMeCl{\cdot}SO_3K$ and PCl_5. This is transformed by $Ba(OH)_2$ at 60—70° into $(CHMeCl{\cdot}SO_3)_2Ba$, which with K_2SO_4 yields $CHMeCl{\cdot}SO_3K$ (**II**), converted by PCl_5 into (**I**). Treatment of (**I**) in Et_2O at 0° with NH_3 produces *α-chloroethanesulphonamide*, m.p. 65—66°, hydrolysed by dil. alkali to MeCHO characterised as its methone condensation product. This conversion presumably takes place through the intermediate formation of $OH{\cdot}CHMe{\cdot}SO_2{\cdot}NH_2$, which in turn is hydrolysed to MeCHO, NH_3, and H_2SO_3. The Cl of (**II**) is not sufficiently reactive to permit the formation of the corresponding OH-compound under the conditions used here. Six compounds derived from MeCHO, each of which contains the C–S linking, are thus described. Treatment of the product (**III**) from MeCHO and $NaHSO_3$ or $KHSO_3$ with conc. NH_3 and subsequent acidification yields $NH_2{\cdot}CHMe{\cdot}SO_3H$, decomp. 260°; NOCl at 0° transforms this into $CHMeCl{\cdot}SO_3H$, neutralised by K_2CO_3 and identified as (**II**). It thus seems clear that (**III**) has the hydroxysulphonate structure since all these reactions are carried out under mild experimental conditions and the possibility of rearrangement seems remote. The HSO_3 compounds are unstable since the reaction which leads to their formation is readily reversible and markedly affected by the presence of acids or alkalis. The C–S linking in them is much more labile than in a simple alkylsulphonic acid. If the initial step in the dissociation results in the formation of the ion $\left[\begin{matrix}H:\ddot{C}:\ddot{O}:H\\ \quad R\end{matrix}\right]^+$ this can easily stabilise itself by loss of a proton to the solvent, H_2O, and thus regenerate the aldehyde. It could also combine with OH^- forming an aldehyde hydrate and thus regenerate the aldehyde. Both reactions would be sensitive to the p_H of the solution. Acetylation of OH would prevent the loss of a proton in this manner and *K α-acetoxyethanesulphonate*, decomp. 209—211° (block), is much more stable than (**III**). In it the SO_3H can be replaced by CN by interaction with CN′ giving $OAc{\cdot}CHMe{\cdot}CN$, b.p. 75—77°/25 mm. H. W.

Action of chloral hydrate on aliphatic ortho-esters. H. W. Post (*J. Org. Chem.*, 1941, **6**, 830—836).—Boiling mixtures of $CCl_3{\cdot}CH(OH)_2$ and the appropriate alkyl orthoformate give the alcohol, formate, and chloral alkyl semiacetal $CCl_3{\cdot}CH(OH){\cdot}OAlk$ in which Alk = Et, Pr, or Bu and O·Alk = SEt. $SiH(OEt)_3$ does not react without formation of gels. $CCl_3{\cdot}CHO$ does not react similarly even in presence of H_2SO_4 as catalyst. The semiacetals have also been obtained by direct action of $CCl_3{\cdot}CH(OH)_2$ and alcohols. Radical interchange can occur between semiacetal and alcohol or orthoformate. H. W.

Nitro- and amino-acetals derived from polyhydric nitro-alcohols.—See A., 1942, II, 111.

Electrolytic reduction of acetone. Factors influencing pinacol formation in alkaline solution. C. L. Wilson and K. B. Wilson (*Trans. Electrochem. Soc.*, 1941, **80**, *Preprint* 30, 377—385).—The amount of pinacol (**I**) produced during the electrolysis of an aq. KOH solution of $COMe_2$, using a Hg cathode, is increased by conditions favouring a high H_2 overvoltage (cf. A., 1942, II, 73). Contrary to the behaviour observed with sorbic acid, however, the formation of (**I**) is increased greatly by increased [KOH] and in 1·82N-KOH the yield is 60%. The results and previous observations on the electrolytic reduction of aldehydes and ketones are discussed with reference to the view that formation of (**I**) is conditioned by adsorption on the cathode. J. W. S.

Thermal reactions promoted by diacetyl.—See A., 1942, I, 105.

Separation of methylamines.—See B., 1941, II, 414.

Interaction of methylamine with nitrous acid. L. U. Spence, F. C. Whitmore, and J. D. Surmatis (*J. Amer. Chem. Soc.*, 1941, **63**, 1771).—NH_2Me does not react with $NaNO_2$ in AcOH. Addition of ~9 or 18% of H_2O causes evolution of 0·5 or 1 mol. of N_2, respectively. In absence of H_2O, decomp. of $NH_2Me{,}HNO_2$ does not occur. R. S. C.

Condensation of amides with carbonyl compounds; benzyl carbamate with aldehydes and α-keto-acids. A. E. Martell and R. M. Herbst (*J. Org. Chem.*, 1941, **6**, 878—887).—The products obtained when various aldehydes are heated with $NH_2{\cdot}CO_2CH_2Ph$ (**I**), usually at 80—110° under diminished pressure, are universally derived from 2 mols. of (**I**) and 1 mol. of aldehyde. Thus are obtained *dicarbobenzyloxy-γ-methylbutylidene-*, m.p. 124°, *-benzylidene-*, m.p. 175°, *-p-methoxybenzylidene-*, m.p. 193°, *-3 : 4-methylenedioxybenzylidene-*, m.p. 204°, and *-furfurylidene-diamine*, m.p. 163°. With α-CO-acids (**II**) the products are derived from 1 or 2 mols. of (**I**) and 1 mol. of (**II**) according to circumstances. Thus $AcCO_2H$ gives *αα-dicarbobenzyloxyamidopropionic acid*, m.p. 139°, whereas $CH_2Ph{\cdot}CO_2H$ affords either *αα-di-*, m.p. 141°, or *α-*, m.p. 160°, *-carbobenzyloxyamido-β-phenylpropionic acid* (**III**). α-Ketoglutaric acid yields *α-carbobenzyloxyamido-α-hydroxyglutarolactone*, m.p. 176°, and $BzCO_2H$ gives *carbobenzyloxybenzylideneimine*, m.p. 240°. (**III**) when heated is transformed into *α-carbobenzyloxyamidocinnamic acid*, m.p. 159°, but the reverse reaction does not take place. Hydrolysis of the condensation products with aq. acid leads to the regeneration of the original aldehyde or CO-acid and (**I**). Catalytic hydrogenation (PdO_2, abs. EtOH) of the condensation products of the aldehydes gives primary amines whilst reduction of the CO-acid derivatives leads to α-NH_2-acids [*anisylamine picrate*, m.p. 190° (decomp.), *piperonylamine picrate*, m.p. 200° (decomp.), and *5-benzyl-3-phenylhydantoin*, m.p. 172°, appear new]. It is suggested that the reaction involves primary addition of the amide to CO followed either by a direct replacement of a OH by another amide residue or by the elimination of H_2O with production of unsaturated intermediates to which a second mol. of amide may add. H. W.

Isomerism of sphingosine sulphate. C. Niemann (*J. Amer. Chem. Soc.*, 1941, **63**, 1763—1764).—Sphingosine sulphate is converted by boiling abs. EtOH containing a drop of conc. H_2SO_4 into a mixture of the original (α-) and less sol., isomeric *β-sphingosine sulphate*. The α- is more rapidly hydrogenated

(PtO_2), less stable in light and air, and more strongly fluorescent than is the β-salt. The α- and β-salts may be *cis*–*trans*-isomerides. R. S. C.

Hofmann degradation of glutaramide. S. R. Aspinall (*J. Amer. Chem. Soc.*, 1941, **63**, 2843).—$NH_2{\cdot}[CH_2]_2{\cdot}NH_2$ (75%) is readily obtained from glutardiamide by aq. Br–KOH at 0°, followed by distillation of the product from aq. KOH. R. S. C.

Transamination reaction. Effect of esterification of the reactants on the mechanism of the reaction. S. D. Brewer and R. M. Herbst (*J. Org. Chem.*, 1941, **6**, 867—877; cf. A., 1937, II, 17).—Transamination takes place in systems in which the CO_2H of both the NH_2- and CO-acid are masked by esterification. The systems $AcCO_2Et$–$NH_2{\cdot}CHPh{\cdot}CO_2Et$ and $BzCO_2Et$–$NH_2{\cdot}CHMe{\cdot}CO_2Et$ have been studied. Transamination in these systems appears to be accomplished by the tautomeric shift of a proton characteristic of the $CH_2{\cdot}N{:}CH$ system. The mobility of the proton is this system is greatly enhanced by the presence of CO_2Et as substituents on the C atoms of the system. This increase in mobility is so great that the tautomeric shift takes place at a conveniently measurable rate even in the absence of a catalyst. In transaminating systems where only one of the CO_2H is masked NH_2 goes to that side of the system carrying the masked CO_2H. The nature of other substituents on the α-C atoms appears to have little influence on the direction of shift of NH_2. *Et benzoylformate* 2 : 4-*dinitrophenylhydrazone* exists in interconvertible dimorphic forms, orange needles, m.p. ~156° (rapid heating), or yellow crystals, m.p. 162—163·5°. H. W.

Dipeptides of unnatural *d*-amino-acids. C. S. Smith and A. E. Brown (*J. Amer. Chem. Soc.*, 1941, **63**, 2605—2606).—*d*-Leucine with HCl–abs. MeOH gives d-*leucine Me* ester *hydrochloride*, m.p. 149—150°, and thence by 33% NaOH–Et_2O the free Me ester (**I**). *Carbobenzyloxy*-d-*phenylalanine*, m.p. 126—128°, $[\alpha]_D^{24}$ −4·6° in AcOH, with PCl_5–Et_2O gives the chloride, which with (**I**) in Et_2O gives N-*carbobenzyloxy*-d-*phenylalanyl*-d-*leucine Me* ester, m.p. 109°; hydrolysis by NaOH–MeOH–H_2O and then hydrogenation (Pd-black; MeOH–H_2O–AcOH) gives d-*phenylalanyl*-d-*leucine* (63%), m.p. 261—262° (decomp.). N-*Carbobenzyloxy*-d-*alanine*, m.p. 84—85°, $[\alpha]_D^{20}$ +13·5° in AcOH, affords, as above, d-*alanyl*-d-*leucine*, +H_2O, m.p. (anhyd.) 254—255° (decomp.). *Carbobenzyloxyglycyl*-, m.p. 101—102°, and *glycyl*-d-*leucine*, yellow at 234°, m.p. 242—243° (decomp.), $[\alpha]_D^{25}$ +35·7° in H_2O (cf. the *l*-isomeride, −35·1±0·5°), are similarly prepared. N-*Carbobenzyloxy*-d-*leucylhydrazide*, m.p. 121°, is described. R. S. C.

Crystalline calcium pantothenate. H. Levy, J. Weijlard, and E. T. Stiller (*J. Amer. Chem. Soc.*, 1941, **63**, 2846—2847).—Cryst-allisation from MeOH or EtOH gives Ca (+)-pantothenate, m.p. 195—196°, $[\alpha]_D^{24}$ +28·2° (+25·8°) in H_2O, solvated but readily obtained solvent-free, and from $Pr^{\beta}OH$ gives a *solvate*, +0·5$Pr^{\beta}OH$ (retained tenaciously), m.p. 200—201°, $[\alpha]_D^{25}$ +25·5° in H_2O, all having full biological potency. Cryst. Ca (−)-pantothenate, m.p. 187·5—189°, $[\alpha]_D^{25}$ −27·8° in H_2O, biologically inactive, is similarly obtained from MeOH. R. S. C.

Amides as hypnotics. III. Disubstituted acetamides. F. F. Blicke and M. F. Zienty (*J. Amer. Chem. Soc.*, 1941, **63**, 2779—2781; cf. A., 1939, II, 62).—The following are prepared by the usual methods. From $CHR(CO_2Et)_2$: *methoxymethylethyl*-, m.p. 91—92° (Et_2 ester, b.p. 115—120°/13 mm.), *ethyl*-β-*methoxyethyl*-, m.p. 121—122° (Et_2 ester, b.p. 135—140°/24 mm.), -β-*ethoxyethyl*-, m.p. 81—82° (Et_2 ester, b.p. 155—160°/22 mm.), -β-*butoxyethyl*-, m.p. 79—80° (Et_2 ester, b.p. 170—175°/25 mm.), -β-*phenoxyethyl*-, m.p. 142—143° (Et_2 ester, b.p. 235—238°/51 mm.), -β-*benzyloxyethyl*-, m.p. 80—81° (Et_2 ester, b.p. 160—165°/2 mm.), -γ-*phenoxypropyl*-, m.p. 97—98° (Et_2 ester, b.p. 243—248°/46 mm.), and -β-β′-butoxyethoxyethyl- (Et_2 ester, b.p. 155—160°/4 mm.), β-*phenylethyl*-β′-*methoxyethyl*-, m.p. 143—144° (Et_2 ester, b.p. 225—230°/31 mm.), -β′-*ethoxyethyl*-, m.p. 146—147° (Et_2 ester, b.p. 210—215°/14 mm.), -β′-*butoxyethyl*-, m.p. 111—112° (Et_2 ester, b.p. 240—245°/34 mm.), -β′-*phenoxyethyl*-, m.p. 188—189° (Et_2 ester, b.p. 245—250°/2 mm.), -γ′-*phenoxypropyl*-, m.p. 185—186° (Et_2 ester, b.p. 185—186°/38 mm.), and -β′-*sec.*-butyl- (Et_2 ester, b.p. 195—198°/12 mm.), phenyl-β-phenoxyethyl- (Et_2 ester, b.p. 208—210°/4 mm.), *di*-(γ-*phenoxypropyl*)-, m.p. 135—136° (Et_2 ester, b.p. 293—296°/11 mm.), α-phenylethylethyl- (Et_2 ester, b.p. 173—175°/4 mm.), and di-(β-β′-butoxyethoxyethyl)- (Et_2 ester, b.p. 220—225°/3 mm.), -malonic acid. Thence at 180° and later 160°: α-methoxymethyl-*n*-butyric acid, b.p. 115—118°/13 mm.; γ-methoxy-, b.p. 145—147°/31 mm. (*amide*, m.p. 101—102°), γ-ethoxy-, b.p. 170—173°/57 mm. (*amide*, m.p. 66—67°), γ-butoxy-, b.p. 145—148°/4 mm. (*amide*, m.p. 55—56°), γ-phenoxy-, b.p. 210—215°/35 mm. (chloride, b.p. 180—185°/35 mm.; *amide*, m.p. 112—113°), γ-β′-butoxyethoxy-, b.p. 185—187°/12 mm., and β-phenyl-, b.p. 165—170°/9 mm. (chloride, b.p. 140—150°/12 mm.; *amide*, m.p. 134—135°), -α-ethyl-*n*-butyric acid; δ-phenoxy-α-ethyl-*n*-valeric acid, b.p. 208—210°/20 mm. (chloride, b.p. 185—190°/24 mm.; *amide*, m.p. 109—110°); γ-methoxy-, b.p. 215—220°/24 mm., γ-ethoxy-, b.p. 244—248°/54 mm. (*amide*, m.p. 93—94°), γ-butoxy-, b.p. 226—230°/57 mm. (*amide*, m.p. 71—72°), and γ-phenoxy-, b.p. 178—180°/5 mm. (*amide*, m.p. 119—120°), -ethyl-α-β′-phenylethyl-*n*-butyric acid; γ-phenoxy-α-phenyl-*n*-butyric acid, m.p. 124—125° (*amide*, m.p. 124—125°); δ-phenoxy-α-γ′-phenoxypropyl-, b.p. 258—260°/48 mm. (chloride, b.p. 208—210°/9 mm.; *amide*, m.p. 89—90°), and α-β′-phenylethyl-β-methyl-*n*-valeric acid, b.p. 185—190°/17 mm. (chloride, b.p. 175—180°/27 mm.; *amide*, m.p. 112—113°); γ-β′-β″-butoxyethoxy-α-β‴-β⁗-butoxyethoxyethyl-*n*-butyric acid, b.p. 223—225°/4 mm. The appropriate alcohol with $SOCl_2$– or PBr_3–C_5H_5N at ≯10° gives β-β′-methoxy-, b.p. 95—97°/59 mm., -*ethoxy*-, b.p. 89—90°/28 mm., and -butoxy-ethoxyethyl chloride, b.p. 195—200°, and the corresponding *bromides*, b.p. —, 108—109°/31 mm., and 115—118°/13 mm., respectively. *o*-$C_6H_4(COCl)_2$ and $NH_2{\cdot}CO{\cdot}NR_2$ at 135° give N-*di-methyl*-, m.p. 144—145°, -*ethyl*-, m.p. 116—117°, and -*butyl-carbamylphthalimide*, m.p. 179—180°, which have no hypnotic activity. The aliphatic amides named above have min. hypnotic and lethal doses (albino rats) 125—2000 and 300—2000 mg. per kg., respectively. R. S. C.

Complex compounds of diguanide with tervalent metals. VIII. Resolution of cobaltic trisdiguanide complex into its optically active enantiomerides. IX. Action of mercuric chloride and silver nitrate on chromium and cobaltic trisdiguanidinium hydroxides, and the constitution of diguanide metallic complexes. P. Rây and S. K. Siddhanta (*J. Indian Chem. Soc.*, 1941, **18**, 289—297, 298—306; cf. A., 1940, II, 208).—VIII. Co^{III} trisdiguanidinium chloride and Ag_2 *d*-tartrate afford *Co*^{III} *trisdiguanidinium chloro*-d-*tartrate* (**I**) (partial racemate) (anhyd. or +H_2O), fractionally crystallised to the l- (**II**) and more sol. d-*forms* (by pptn. with EtOH), which are anhyd. when heated at 62°, and with $(NH_4)_2SO_4$ give l- and d-*Co*^{III} *trisdiguanidinium sulphate*, respectively, and thence [$BaCl_2$ or $Ba(NO_3)_2$] the respective *chlorides* and *nitrates*. (**II**) only is obtained when (**I**) is fractionally crystallised slowly in the cold and this is the first case of a complex inorg. salt showing " asymmetric transformation of the second order " (cf. Kuhn, A., 1932, 269). l- and d-*Co*^{III} *trisdiguanidinium* d-*camphorsulphonate* are obtained by crystallising the corresponding partial racemate (*loc. cit.*). r-*Co*^{III} *trisdiguanidinium* d-*tartrate* affords the l- and more sol. d-*forms* similarly. Many vals. of $[\alpha]_D$ are given.

IX. Cr^{III} trisdiguanide monohydrate and warm aq. $HgCl_2$ yield *Cr*^{III} *trisdiguanide mercurichloride*, $Cr(C_2H_5N_5{\cdot}HgCl)_3$ (anhyd. or +H_2O). Co^{III} diguanide hydrate and aq. $HgCl_2$ at 100° (bath) afford the double *compound*, $Co(C_2H_5N_5{\cdot}HgCl)_3{,}HgCl_2$; diguanide hydroxide and aq. $HgCl_2$ (cold) give *diguanide mercurichloride*, $(C_2H_5N_5){\cdot}2HgCl$. A dil. solution of $(CH_2{\cdot}NH_2)_2$, added slowly to conc. aq. $HgCl_2$ at room temp. affords the *complex*, $2(CH_2{\cdot}NH{\cdot}HgCl)_2{,}HgCl_2{,}7H_2O$. Cr^{III} or Co^{III} trisdiguanide hydrochloride and cold aq. $HgCl_2$ give the double *compounds* [Cr or $Co(C_2H_7N_5)_3]Cl_3{,}3HgCl_2$ (+$2H_2O$ in Co compound). Trisethylenediamine Co^{III} hydroxide and aq. $HgCl_2$ give an unstable product, changing readily into $2HgO{,}HgCl_2$, and a *compound*, (**III**) $\{Co[(CH_2{\cdot}NH_2)_2]_3\}Cl_3{,}5HgCl_2{,}2H_2O$. Trisethylenediamine Co^{III} chloride and cold aq. $HgCl_2$ give a double salt of the same empirical composition as (**III**). Co^{III} trisdiguanide hydrate and cold aq. $AgNO_3$ afford *Co*^{III} *diguanide Ag hydroxide*, $Co(C_2H_6N_5{\cdot}AgOH)_3$(+ some H_2O) (structure suggested). A. T. P.

Nickel diguanides.—See A., 1942, I, 111.

Catalytic hydrogenation of higher aliphatic nitriles.—See B., 1941, II, 414.

Optically active α-bromopropionitrile. K. L. Berry and J. M. Sturtevant (*J. Amer. Chem. Soc.*, 1941, **63**, 2679—2680).—Partly resolved CHMeBr·CO_2H, $[\alpha]_D^{25}$ −13·79°, is converted successively into the chloride, $[\alpha]_D^{20}$ −11·7°, amide, $[\alpha]_D^{24}$ −12·9°, nitrile (**I**), m.p. −63·4° (corr.), b.p. 44·5°/15 mm., $[\alpha]_D^{21}$ −7·35°, and Et ester, b.p. 60—61°/21 mm., $[\alpha]_D^{23}$ −5·09°. $[\alpha]_D^{25}$ for pure (**I**) is calc. to be between −23·1° and −15·5°. The rototary dispersion of (**I**), *d*, refractive dispersion, and absorption (λ 0·420—0·220 × 10^{-6} mm.) of *dl*-(**I**) are recorded. R. S. C.

Addition of hydrogen bromide to α-ethoxyacrylonitrile. C. C. Price, E. C. Coyner, and D. DeTar (*J. Amer. Chem. Soc.*, 1941, **63**, 2796—2798).—OEt·CHBr·CH_2Br (prep. by bromination of OEt·CHMeCl), b.p. 75—79°/20 mm., and CuCN in abs. Et_2O give *β-bromo-α-ethoxypropionitrile* (~50%), b.p. 62—63°/4 mm., which with C_5H_5N–Et_2O at 0° gives *α-ethoxyacrylonitrile* (**I**), f.p. −49·6°, b.p. 133—135°/760 mm., 63°/60 mm. (40% over-all yield if isolation of intermediates is omitted). With 1—1·5 mols. of HBr, (**I**) gives *α-bromo-α-ethoxypropionitrile* (**II**) (75—95%), lachrymatory, b.p. 44—45°/13 mm., which resists polymerisation, loses HCN and HBr quantitatively, and is hydrolysed vigorously by H_2O to HCN, HBr, EtOH, AcOH, and traces of EtOAc. Use of <2 mols. of HBr gives mixtures of mono- and di-hydrobromides of (**II**), also obtained from (**II**) and HBr. Some CH_2Br·CH(CN)·OEt is formed as well as (**II**). R. S. C.

Photolysis of azomethane.—See A., 1942, I, 109.

II.—SUGARS AND GLUCOSIDES.

Distillation of sugar propionates at low pressures. C. D. Hurd, R. W. Liggett, and K. M. Gordon (*J. Amer. Chem. Soc.*, 1941, **63**, 2656—2657).—Apparatus is described for distillation at 0·1—0·001 mm. of propionates of mono-, di-, or tri-saccharides, which is usually more satisfactory than that of the acetates. R. S. C.

Propionates of sugars. C. D. Hurd and K. M. Gordon (*J. Amer. Chem. Soc.*, 1941, **63**, 2657—2659).—The following are prepared by $(EtCO)_2O$–C_5H_5N at room temp. and purified by distillation: L-*rhamnose*, a syrup, [α] −43°, L-*arabinose*, m.p. 80°, [α] +116°, and D-*xylose tetrapropionate*, m.p. 42—43°, [α] +43°; D-*fructose*, [α] +24°, D-*mannose*, [α] +24°, D-*galactose*, [α] +54°, and L-*sorbose pentapropionate*, all syrups, [α] −17°; *maltose*, m.p. 144°, [α] +55°, *cellobiose*, m.p. 170°, [α] +8·0°, *lactose*, a syrup, [α] +32°, *sucrose*, m.p. 45—46°, [α] +53°, *gentiobiose*, m.p. 151—152°, [α] −3·3°, *trehalose*, m.p. 52—53°, [α] +144°, melibiose, a syrup, [α] +92°, and neolactose octapropionate, a syrup, [α] −4·5°; *raffinose hendecapropionate*, a syrup, [α] +95°. Maltose octaacetate having m.p. 155—156° is obtained by distillation. [α] are $[\alpha]_D^{20}$ in $CHCl_3$. R. S. C.

Analytical separation of sugars by distillation of their propionates. C. D. Hurd and R. W. Liggett (*J. Amer. Chem. Soc.*, 1941, **63**, 2659—2662).—The following mixtures are analysed by fractional distillation of the propionates (see above): glucose–maltose, glucose–trehalose–lactose–raffinose, glucose–sucrose–raffinose, glucose–maltose–raffinose, and glucose–fructose–sucrose–raffinose. The accuracy is 1—2% for mono- and 2—4% for di- or tri-saccharides. A correction is needed for fructose. R. S. C.

Action of hydrogen peroxide in *tert.*-butanol on *D*-arabinal, *D*-galactal, and their acetates in presence of osmium tetroxide. R. C. Hockett and (Miss) S. R. Millman (*J. Amer. Chem. Soc.*, 1941, **63**, 2587—2589).—With H_2O_2–OsO_4 in Bu^{t}OH (cf. A., 1941, II, 352), *D*-arabinal (~3 g.) gives *D*-arabinose (17·3%; isolated partly as such and partly as benzylphenylhydrazone) and *D*-erythronic acid (0·33 g.; isolated as Ca salt). Similar oxidation of *D*-arabinal diacetate gives, after hydrolysis, 30% and a trace, respectively. *D*-Galactal (1·3246 g.) and its triacetate (2·0478 g.) give *D*-galactose 52·9 and 42·4% and ? *D*-lyxonic acid 0·35 and 0·053 g., respectively. Ribose and talose are not formed. R. S. C.

Carbohydrate sulphuric esters. II. Isolation of 3 : 6-anhydromethylhexosides from methylhexopyranoside sulphates. R. B. Duff and E. G. V. Percival (*J.C.S.*, 1941, 830—833; cf. A., 1941, II, 34).—*Ba α-* and *β-methylgalacto-*, $[\alpha]_D^{17}$ −12° in H_2O, *α-*, $[\alpha]_D^{17}$ +81° in H_2O, and *β*-methylgluco-, $[\alpha]_D^{20}$ −12° in H_2O, and *α-methylmanno-pyranoside sulphate*, $[\alpha]_D^{18}$ +38° in H_2O (from the methylhexoside and 1 mol. of $ClSO_3H$ in C_5H_5N), are hydrolysed [$Ba(OH)_2$ at 100°] to 3 : 6-anhydro-*α-* and *-β*-methylgalacto-, *-α-* (**I**) [methylated (MeI + Ag_2O) to the 2 : 4-Me_2 derivative; converted by N-H_2SO_4 at room temp. into the furanoside, and in the hot into 3 : 6-anhydroglucose] and *β*-methylgluco- and *α*-methylmanno-pyranoside, with small amounts of the methylhexoside. The first three are also prepared [with the -furanoside in the case of (**I**)] from the methylhexoside without isolation of the Ba salt. (**I**) in excess of $Ba(OH)_2$ with $ClSO_3H$ in C_5H_5N gives the corresponding furanoside (good yield). (**I**) and *α*-methylglucoside are unaffected by boiling $Ba(OH)_2$. The anhydromethylhexosides previously reported (*loc. cit.*) as derived from *α*-methylgalactoside were impure (**I**) due to contamination of galactose with glucose. A. Li.

Crystalline α-methyl-*D*-altroside and derivatives of *D*-altrose. N. K. Richtmyer and C. S. Hudson (*J. Amer. Chem. Soc.*, 1941, **63**, 1727—1731).—Altrosan and Ac_2O–C_5H_5N at 0° and later room temp. give the 2 ; 3 : 4-*triacetate*, m.p. 100—101°, [α] −172° in $CHCl_3$, converted by H_2SO_4–Ac_2O into the *β-* (36% calc.) and *α-penta-acetate* (**I**) (64% calc.; 57% isolated), m.p. 118—119°, [α] +63·0° in $CHCl_3$. With $TiCl_4$ in $CHCl_3$ at 70—75°, (**I**) or the crude α + *β*-mixture gives *α-acetochloro*-D-*altrose*, m.p. 101—102°, [α] +110·0° in $CHCl_3$, which with Ag_2CO_3 in $COMe_2$–H_2O gives *β*-D-*altrose* 2 : 3 : 4 : 6-*tetra-acetate*, m.p. (anhyd.) 85—90°, (+$COMe_2$) 65°, [α] −6·0° → +12·9° in 6 weeks in $CHCl_3$. With MeI–Ag_2O at ~2° this gives *β-* (**II**), m.p. 94—95°, [α] −61·0° in $CHCl_3$, and *α-methyl*-D-*altroside tetra-acetate* (**III**), m.p. 88—89°, [α] +66·0° in $CHCl_3$. $TiCl_4$–$CHCl_3$ at 70° converts (**II**) into a mixture of (**III**) (64%) and (**II**) (36%). 4 : 6-Benzylidene-α-methylglucoside, m.p. 163—164°, [α] +110·4° in $CHCl_3$, gives the 2 : 3-di-*p*-toluenesulphonate, forms, m.p. 147—148° and (unstable) 132—133°, [α] +11·8° in $CHCl_3$ (and, in one experiment, the 2-*p*-toluenesulphonate, m.p. 152—153°, [α] +64·5°), converted by NaOMe–MeOH–$CHCl_3$ at 0° into 4 : 6-benzylidene-α-methyl-2 : 3-anhydro-*D*-alloside, m.p. ~200° (varies with the rate of heating), [α] +140° in $CHCl_3$. With boiling aq. KOH this gives 4 : 6-benzylidene-*α-* (**IV**), m.p. 169—170°, [α] +115·0° in $CHCl_3$, and a little *-β*-methyl-*D*-altroside, m.p. 163—164°, [α] +110·0° in $CHCl_3$. Hydrolysis of (**III**) by $Ba(OMe)_2$ or of (**IV**) by N-H_2SO_4 at 60° gives α-methyl-*D*-altropyranoside, m.p. 107—108°, [α] +125·8±0·5° in H_2O, +135·1° in MeOH, the structure of which is shown by oxidation by $NaIO_4$ or HIO_4 (2 equivs. consumed) to HCO_2H (1 mol.) and an aldehyde, oxidised by Br–aq. $SrCO_3$ to Sr *D'*-methoxy-*D*-hydroxymethyldiglycollate, +$2H_2O$. [α] are $[\alpha]_D^{20}$. R. S. C.

Sugar acetates, acetylglycosyl halides and orthoacetates in relation to the Walden inversion. H. L. Frush and H. S. Isbell (*J. Res. Nat. Bur. Stand.*, 1941, **27**, 413—428).—The tendency of Ac groups in sugar acetates and glycosyl halides to form intramol. condensation products depends on the stereochemical arrangement of groups. Formation of orthoesters is discussed in relation to the opposite-face concept for the Walden inversion, and it is shown that orthoacetates are formed when an Ac can approach the face of a neighbouring C opposite to a replaceable halogen. *α-d-α*-Guloheptose and Ac_2O–C_5H_5N at 0° for 2 days give α-d-*α-guloheptopyranose hexa-acetate*, m.p. 126°, $[\alpha]_D^{20}$ −62·8°, converted by HBr–Ac_2O at 0° into α-d-*α-bromoguloheptopyranose penta-acetate*, m.p. 139—140°, $[\alpha]_D^{20}$ −124°, which with Ag_2CO_3–CaSO$_4$–MeOH at 0° yields (almost quant.) d-*α-guloheptose Me* 1 : 2-*orthoacetate tetra-acetate*, m.p. 106°, $[\alpha]_D^{20}$ +3·2° [0·1N-HCl in $CHCl_3$ gives (?) *α-d-α*-chloroguloheptose penta-acetate]. *α*-Chloroneolactosyl hepta-acetate similarly (Koenigs-Knorr reaction) affords *neolactose Me* 1 : 2-*orthoacetate hexa-acetate*, m.p. 121—122° $[\alpha]_D^{20}$ +25·3° (70% yield) (0·1N-HCl–$CHCl_3$ yields *α*-chloroneolactose hepta-acetate), and *methyl-β-neolactopyranose hepta-acetate*, m.p. 179°, $[\alpha]_D^{20}$ −14·5° (30% yield) (does not react with HCl–$CHCl_3$). Photomicrographs of the new compounds are shown. A. T. P.

Synthesis of the epimerides of cellobiose (4-*β*-*D*-glucopyranosido-*D*-mannose). W. T. Haskins, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1941, **63**, 1724—1726).—2 : 3-*iso*Propylidene-*D*-mannosan <1 : 5>*β*<1 : 6>, acetobromoglucose, Ag_2O, and $CaSO_4$ in $CHCl_3$ at 20° give 24—32% of 2 : 3-iso*propylidene*-4-2′ : 3′ : 4′ : 6′-*tetra-acetyl*-*β*-D-*glucosido*-D-*mannosan* <1 : 5>*β*<1 : 6>, m.p. 176°, [α] −50·0°, hydrolysed by 80% AcOH at 100° to 4-2′ : 3′ : 4′ : 6′-*tetra-acetyl*-*β*-*glucosido*-D-*mannosan* <1 : 5>*β*<1 : 6>, m.p.

192—193°, [α] −68·9°. With Ac_2O–C_5H_5N at room temp. this gives the *mannosan* 2 : 3 : 2′ : 3′ : 4′ : 6′-*hexa-acetate*, m.p. 131—132°, [α] −69·8°, converted by H_2SO_4–Ac_2O–AcOH into 4-β-*D*-glucosido-α-*D*-mannose octa-acetate, m.p. 199—200° (lit. 202—203°), [α] +36·5°, and thence into the free disaccharide. M.p. are corr. [α] are $[\alpha]_D^{20}$ in $CHCl_3$. R. S. C.

Heart glycosides. XVII. Transformation of scillaren-*A* into *epiallo*lithocholic acid [3-β-hydroxy*allo*cholanic acid]. A. Stoll and J. Renz (*Helv. Chim. Acta*, 1941, **24**, 1380—1388; cf. A., 1935, 754).—Hydrogenation of scillaren *A* (I) (H_2–PtO_2 in MeOH–EtOH) gives hexahydrodeoxyscillarenic acid *A*, m.p. 212—215° (decomp.), $[\alpha]_D^{20}$ −43·6° in EtOH, in very variable yield (cf. A., 1935, 330). Under the influence of HCl in abs. EtOH it readily loses the sugar residue and *tert.*-OH at $C_{(14)}$, giving a singly unsaturated OH-acid which is immediately hydrogenated to a mixture of stereoisomeric acids from which *epiallo*lithocholic [3-β-hydroxy*allo*cholanic] acid, m.p. 220°, $[\alpha]_D^{20}$ +23° in EtOH, is extracted by means of the Me ester, m.p. 150—151°, $[\alpha]_D^{20}$ +23° in EtOH, +18° in $CHCl_3$ (acetate, m.p. 155°, $[\alpha]_D^{20}$ +14° in EtOH). (I), scillaridin *A*, and anhydroscillaridin *A* have the structures (I), (II), and (III).

(I.) $C_{12}H_{21}O_9{\cdot}O$– (R, OH)

(II.) (R, OH)

(III.) (R) [R = ·C(CH—O)(CH:CH)CO]

H. W.

Verbenalin. E. Bureš and D. Šusterová-Říhová (*Časopis Československ. Lék.*, 1938, **18**, 65—69).—Verbenalin is isolated by a new method in a state of greater purity, m.p. 183°, $[\alpha]_D^{20}$ −180·6°. When hydrolysed by 9% H_2SO_4 it gives *d*-glucose and verbenalol, m.p. 131°, equal to that obtained by Cheymol (A., 1936, 1366) by hydrolysis with emulsin. F. R.

Preparation of purpurogallase.—See A., 1942, III, 266.

Polysaccharide associated with β-amylase. L. H. Ford and S. Peat (*J.C.S.*, 1941, 856—864).—The *polysaccharide* (I), $[\alpha]_D^{20}$ −78·5° in H_2O, associated with β-amylase in ungerminated wheat flour is isolated as the *acetate*, $[\alpha]_D^{14}$ −57·7° in $CHCl_3$, after fractional pptn. by EtOH from the 20% aq. EtOH extract. Different fractions of the *methylated polysaccharide* have $[\alpha]_D$ −75° to −128° in $CHCl_3$, but all with 4% MeOH–HCl, then dil. aq. HBr, yield trimethyl-*l*-arabofuranose (6 mols.), 2 : 3-dimethylxylose (6 mols.), 2-methylxylose (1 mol.), xylose (1 mol.), and 2 : 4-dimethylgalactose (1 mol.). (I) has no amylolytic activity. Its constitution is discussed. A. Li.

Constitution of yeast mannan. W. N. Haworth, R. L. Heath, and S. Peat (*J.C.S.*, 1941, 833—842).—Earlier work (A., 1937, II, 277) is confirmed. The trimethylmannose fraction of the products of hydrolysis (AcOH–5% HCl at 100°) of the methylated mannan contains 2 : 3 : 4- (1—10%), 3 : 4 : 6- (45%) [*anilide*, m.p. 140—143°, $[\alpha]_D^{18}$ +154·5° → −55·5° (24 hr.) in MeOH; amide, m.p. 143°, $[\alpha]_D^{18}$ +28° in H_2O], and 2 : 4 : 6-trimethylmannose ($+H_2O$), m.p. 90°, $[\alpha]_D^{18}$ +21° → +14° (2 hr.) in H_2O (partly converted at 100° into the anhyd. *β-form*, m.p. 104—107°, $[\alpha]_D^{20}$ −5·7° → +19·0° in H_2O) [anilide, m.p. 134°, $[\alpha]_D^{20}$ −150° → +8° (13 hr.) in MeOH], which with 2% MeOH–HCl yields the α-methylmannoside, methylated to tetramethyl-α-methylmannoside, and with Br–H_2O, 2 : 4 : 6-*trimethylmannonolactone* (I), m.p. 97—98°, $[\alpha]_D^{20}$ +141° → +30° (103 hr.) in H_2O. The *amide*, m.p. 145°, $[\alpha]_D^{20}$ +7·0° in H_2O, of (I) gives a negative Weerman test for α-OH-amides. Methylation (MeI–Ag_2O) of (I) and treatment with $NHPh{\cdot}NH_2$ yields 2 : 3 : 4 : 6-tetramethylmannonic acid phenylhydrazide. 3 : 4-Dimethyl-δ-mannonolactone [from dimethylmannose monohydrate (II) (*loc. cit.*)] has m.p. 159—160°, $[\alpha]_D^{15}$ +178° → +131° (120 hr.) in H_2O, and the amide from it, $[\alpha]_D^{19}$ +25·7° in H_2O, gives a positive Weerman test. With $COMe_2$ (H_2SO_4), (II) yields 1 : 2-*isopropylidene*-3 : 4-*dimethylmannose*, m.p. 94°, $[\alpha]_D^{16}$ −17° in H_2O, methylated to 3 : 4 : 6-trimethylmannose. The constitution of yeast mannan is discussed in terms of 30—60 repeating units of 6 mannose residues each. A. Li.

Starch. XV. Kinetics of the degradation of non-degraded potato and maize starch by β-amylase. K. H. Meyer, E. Preiswerk, and R. Jeanloz (*Helv. Chim. Acta*, 1941, **24**, 1395—1400).—Potato starch is degraded rather more rapidly than maize starch and both are more resistant than sol. starch (I). With higher concn. of starch the val. of $V = v/E$ (v = rate of reaction and E = concn. of enzyme) decreases for some unexplained reason although theoretically it should tend towards an upper limit. This phenomenon has been observed previously with (I). Constancy of V with variable concn. of enzyme and const. concn. of substrate is realised only in presence of a large excess of the latter. At lower concn. of substrate V increases with diminution of E. Solutions of starch age much more slowly than those of amylose. The energy of activation is ~10,000 g.-cal. at 20°. H. W.

Starch. XVI. Degradation of carbohydrates of the starch group by Lebedev's extract of dried yeast. K. H. Meyer and P. Bernfeld (*Helv. Chim. Acta*, 1941, **24**, 1400—1403).—It appears that the extract does not contain an α-amylase similar to other animal or vegetable amylases since it loses its entire activity when heated at 70° or submitted to p_H 3·6, whereas under the same conditions α-amylase is heat-resistant and β-amylase is unaffected by acidity. The extract, highly active towards maltose (I), has a distinct hydrolysing action towards the various carbohydrates of the starch group. Since partial deactivation, caused either by heat-treatment or acidity, weakens the reaction to the same extent towards (I) and towards glycogen (II) it appears probable that the enzyme is the same in each case. The possibility of two different reactions is not, however, excluded; one of them towards (I) is purely hydrolytic (α-glucosidase) whereas the other is that of phosphorylase followed by phosphomutase on the polysaccharides. This last action would give rise to a hexose phosphate with free ·CHO. Under similar conditions maize amylase, Zulkowski's sol. starch, residual dextrins of maize starch, and (II) are hydrolysed to the extent of 3·85, 6·6, 16·2, and 24·8%, respectively, the corresponding content of terminal groups being 0·4, 4, 8·9, and 9%. Apparently the enzyme attack the ends of the chains in the first instance. H. W.

Starch. XVII. Starch of glutinous rice. K. H. Meyer and M. Fuld (*Helv. Chim. Acta*, 1941, **24**, 1404—1407).—Ordinary rice (I) yields to cold H_2O small amounts of a carbohydrate which gives a pale reddish colour with I and appears identical with that derived from glutinous rice (II). Extraction of (I) with H_2O at 40° or, preferably, at 65° gives amylose identical with the crude amylose derived from potato or rice starch. The starch grains obtained by repeated levigation of (II) are birefractive and of the same size as those derived from (I). They are microcryst. The first swelling of (II) is observed at 55° and at 65° the granules pass into a cloudy suspension which has no longer the properties of a starch. Simple treatment with warm H_2O dissolves a substance which gives a red colour with I; part of this is solubilised in course of the prep. of starch by levigation. Complete extraction of the carbohydrate (III) is obtained at 40° and it is obtained in 1·6% yield by pptn. with EtOH. The reducing power of (III) indicates a chain length of ~20 glucose units. It is degraded by β-amylase to the extent of 47%. (III) appears therefore to be highly branched and allied to glycogen (IV). Aq. extraction of the grains at 50°, 60°, and 70° invariably gives quantities of carbohydrate which gives a red colour with I. There are no H_2O-sol. portions which give a blue colour. Also there is no slow separation of cryst. amylose. The total carbohydrate contains 6% of terminal groups but this includes those of the amylopectin and (IV). Degradation by β-amylase affords 40% of residual dextrin. H. W.

Molecular constitution of glycogen and starch from the seed of sweet corn (*Zea mays*). W. Z. Hassid and R. M. McCready (*J. Amer. Chem. Soc.*, 1941, **63**, 1632—1635).—End-group analysis confirms the structure of the glycogen (12 units) and starch (25 units) from this seed (cf. Morris *et al.*, A., 1939, III, 1112). R. S. C.

Acid nature of cellulose.—See A., 1942, I, 59.

Effect of ultra-violet light on methylcellulose in solution.—See A., 1942, I, 109.

Mesylated cellulose [cellulose methanesulphonate] and derivatives. M. L. Wolfrom, J. C. Sowden, and E. A. Metcalf (*J. Amer. Chem. Soc.*, 1941, **63**, 1688—1691).—Cotton linters, activated by 18% NaOH or regenerated from an acetate, with 3 or 6 mols. of $MeSO_2Cl$ in C_5H_5N at 0° and later room temp. gives a product (**I**) containing 1·7 $MeSO_2$ after ~2 and 8 days, respectively, the $MeSO_2$ content later decreasing. At higher temp. darkening occurs. Cellulose acetate and $MeSO_2Cl$ at room temp. give a product (**II**) containing 1·72 Ac and 1·03 $MeSO_2$, which in C_5H_5N–C_5H_5N,HCl at 80—85° gives a powder containing Cl. With NaI in boiling $(CH_2Ac)_2$ (milder conditions lead to incomplete removal of $MeSO_2$), 0·4 I is introduced into (**II**) in place of 1 $MeSO_2$. With 28—29% aq. NH_3 at room temp., (**I**) and (**II**) give material containing 3—6% of Cl and 0·5—4% of N. R. S. C.

III.—HOMOCYCLIC.

Common basis of intramolecular rearrangements. VIII. Formation of *cyclo*propanes from monohalides and sodium. II. 1 : 1 : 2-Trimethyl*cyclo*propane from α-chloro-ββ-dimethylbutane. F. C. Whitmore and T. P. Carney (*J. Amer. Chem. Soc.*, 1941, **63**, 2633—2635; cf. A., 1941, II, 89).—Addition of Na to $CMe_2Et{\cdot}CH_2Cl$ at 55—70° gives exothermally CMe_3Et (29), 1 : 1 : 2-trimethyl*cyclo*propane (**I**) (13), b.p. 56·5—57·5°/735 mm., and $CH_2{:}CHBu^\gamma$ (8%), reaction (probably bimol.) being by way of $CMe_2Et{\cdot}CH_2{\cdot} \rightleftharpoons {\cdot}CHMeBu^\gamma$ and no rearrangement occurring. $CH_2Ac{\cdot}CMe_2{\cdot}OH$ with H_2–catalyst gives $OH{\cdot}CHMe{\cdot}CH_2{\cdot}CMe_2{\cdot}OH$, converted by aq. HBr at 60° into $CHMeBr{\cdot}CH_2{\cdot}CMe_2Br$, addition of which to NH_2Ac–Na_2CO_3–NaI–Zn dust at 155° gives (**I**), b.p. 55·5—56·5°/735 mm. There is no immediate reaction between (**I**) and $KMnO_4$. R. S. C.

Preparation of *cyclo*propene. M. J. Schlatter (*J. Amer. Chem. Soc.*, 1941, **63**, 1733—1737; cf. A., 1923, i, 1192; 1930, 331).—$Cl{\cdot}[CH_2]_3{\cdot}Br$ and NaCN in warm 96% EtOH give exothermally $Cl{\cdot}[CH_2]_3{\cdot}CN$ (67·5%), b.p. 94°/26 mm., $+Br{\cdot}[CH_2]_3{\cdot}CN$ (32·5%; 47% prepared from $Br{\cdot}[CH_2]_3{\cdot}Br$ in aq. EtOH), b.p. 108°/26 mm., which with $NaNH_2$ gives 61% of *cyclo*propyl cyanide (**I**), b.p. 69—70°/80 mm. With boiling, aq. KOH, (**I**) gives 96% of the acid (**II**), b.p. 80—81°/13 mm., the amide (**III**), m.p. 125°, of which is also obtained (85%) from (**I**) by HCl–EtOH. Br–NaOMe rearranges (**III**) to aceto*cyclo*propylamide (68%), hydrolysed to *cyclo*propylamine (**IV**) (80%), b.p. 49—50°/750 mm., also obtained (25%) with some (?) N-*carbocyclopropyloxy*·N′-*cyclopropylcarbamide*, m.p. 100°, from (**II**) by NaN_3–H_2SO_4–$CHCl_3$ at 35—40°. MeI–KOH–MeOH converts (**IV**) into *cyclopropyltrimethylammonium iodide* (**V**) (83%), m.p. 274° (decomp.), which with AgOH gives the hydroxide, pyrolysed (Pt–asbestos) at 320—330° to *cyclo*propene (45%), b.p. −36° to −35°/744 mm., unstable even at −78°, and *cyclo*propyldimethylamine (30%), b.p. 60·1°/748 mm. [with MeI gives (**V**); picrate, m.p. 196·5° (decomp.)]. The products of pyrolysis contain some $CH{:}CMe$ and the crude products with Br yield 1 : 2-*dibromocyclopropane* (**VI**), m.p. −1° to 1°, b.p. 57—58°/50 mm., with some $CHBr_2{\cdot}CMeBr_2$, b.p. 110—112°/10 mm., and $CH_3(CHBr_2)_2$, b.p. 122—123°/10 mm. Zn–EtOH converts (**VI**) mainly into *cyclo*propane (cf. *loc. cit.*). R. S. C.

Preparation and vapour pressures of *cyclo*butene and *cyclo*butane. G. B. Heisig (*J. Amer. Chem. Soc.*, 1941, **63**, 1698—1699).—*cyclo*Butanecarboxylic acid with NaN_3–H_2SO_4–$CHCl_3$ at 40—50° and later KOH gives 92% of *cyclo*butylamine. Addition of 1 : 2-dibromo*cyclo*butane to Zn dust in boiling EtOH gives 96% of *cyclo*butene (**I**). The v.p. of (**I**) (purification described) from −77·1° to 2·4° is given by $\log_{10} P_{mm.} = 7{\cdot}5728 - 1292{\cdot}7/T$ and that for *cyclo*butane (purification described) from −74·4° to 13·08° by $\log_{10} P = 7{\cdot}5330 - 1328{\cdot}9/T$. R. S. C.

Alkyl and *cyclo*alkyl derivatives of 1 : 3-diphenyl-1 : 3-dimethyl*cyclo*butane.—See B., 1941, II, 414.

Bromination of *cyclo*hexane, methyl*cyclo*hexane, and *iso*butane.—See A., 1942, II, 69.

Oxygen effect in reaction of bromine with *tert.*-butylbenzene.—See A., 1942, II, 70.

Di*cyclo*pentadiene : preparation from the monomeride ; dielectric constants of dimeride at several temperatures. C. E. Waring, E. E. Kern, and W. A. Blann (*J. Amer. Chem. Soc.*, 1941, **63**, 1767).—When the fraction of b.p. 40—44° obtained by distilling 98%-pure di*cyclo*pentadiene is kept at 15—20° and then freed from monomeride in vac., there is obtained a *form*, m.p. 27·8°, of di*cyclo*pentadiene, which after melting resolidifies to the known form, m.p. 31·5°. The dipole moment at 40° to 100° is 2·43 to 2·31. R. S. C.

Photochemical decomposition of benzene.—See A., 1942, I, 109.

Mercury-photosensitised reactions involving benzene and hydrogen.—See A., 1942, I, 109.

Effect of organic peroxides in chlorination reactions.—See A., 1942, II, 69.

Action of elementary fluorine on organic compounds. XI. Vapour-phase fluorination of benzene. N. Fukuhara and L. A. Bigelow (*J. Amer. Chem. Soc.*, 1941, **63**, 2792—2795).—No aromatic products are obtained from C_6H_6 and F_2–N_2 in presence of Cu gauze at ~90°. The products are CF_4 (much), C_2F_6, C_4F_{10}, b.p. −2°, C_5H_{10}, b.p. 0—1°/330 mm., 22°/760 mm., dodecafluoro*cyclo*hexane, m.p. 48—49°, b.p. 50°, *undecafluoro*cyclo*hexane*, b.p. 62° (*forms*, m.p. 41—43° and −16° to −14° in mobile equilibrium), and ? *di*(*undecafluoro*cyclo*hexyl*), m.p. 19—21°, b.p. 90°/90 mm. They are probably formed by a free radical mechanism, involving first addition of F_2 and then substitution, followed by ring-crumpling with emission of small fragments (CF_3). R. S. C.

Manufacture of ethylbenzene.—See B., 1941, II, 415.

Organic reactions with boron fluoride. XXV. Preparation of *p*-dialkylbenzenes. C. E. Welsh and G. F. Hennion (*J. Amer. Chem. Soc.*, 1941, **63**, 2603—2604).—Condensation of PhMe or PhEt with, preferably *n*-C_{4-12}, alcohols and BF_3 or BF_3–P_2O_5 gives good yields of *p*-dialkylbenzenes, the longer alkyl being *sec.* In the experiments detailed below, 1 mol. of BF_3 is used; the mol. amount of P_2O_5 (if any), temp. (±5°), and time of reaction are given in parentheses. (*a*) PhMe : EtOH (P_2O_5 0·25; BF_3 1·2 mol.; 90—115°; 22 hr.) gives (mainly *p*-)C_6H_4MeEt (70%); $Pr^\alpha OH$ (P_2O_5 0·25; 70°; 9 hr.) gives *p*-$C_6H_4MePr^\beta$ (76%), b.p. 175°/740 mm.; $Bu^\alpha OH$ (P_2O_5 0·25; 70°; 3 hr.) gives *p*-$C_6H_4Me{\cdot}CHMeEt$ (90%), b.p. 193°/732 mm.; $Bu^\beta OH$ (75°; 4·5 hr.) gives *p*-$C_6H_4MeBu^\gamma$ (65%), b.p. 188—189°/740 mm.; *n*-$C_5H_{11}{\cdot}OH$ (P_2O_5 0·25; 75°; 6 hr.) gives p-α-*methyl*-n-*butyltoluene* (81%), b.p. 95°/20 mm.; *n*-$C_8H_{17}{\cdot}OH$ (P_2O_5 0·25; 75°; 2 hr.) gives p-α-*methyl*-n-*heptyltoluene* (81%), b.p. 116°/7 mm.; *n*-$C_{12}H_{25}{\cdot}OH$ (P_2O_5 0·25; 80°; 2 hr.) gives p-α-*methyl*-n-*undecyltoluene* (81%), b.p. 167°/8 mm.; *n*-$C_{16}H_{33}{\cdot}OH$ (P_2O_5 0·25; 85°; 12 hr.) gives p-α-*methyl*-n-*heptadecyltoluene* (17%), b.p. 234—237°/8 mm.; *cyclo*hexanol (75°; 1·5 hr.) gives *p-cyclo*hexyltoluene (81%), b.p. 117°/10 mm. (*b*) PhEt + P_2O_5 0·25 mol. : $Pr^\alpha OH$ (80°; 4 hr.) gives *p*-$C_6H_4EtPr^\beta$ (81%), b.p. 193°/744 mm.; $Bu^\alpha OH$ (75°; 4 hr.) gives p-*ethyl*-sec.-*butylbenzene* (96%), b.p. 86°/16 mm.; *n*-$C_5H_{11}{\cdot}OH$ (75°; 5 hr.) gives p-*ethyl*-α-*methyl*-n-*butylbenzene* (79%), b.p. 97°/11 mm.; *n*-$C_8H_{17}{\cdot}OH$ (75°; 8 hr.) gives p-*ethyl*-α-*methyl*-n-*heptylbenzene* (64%), b.p. 126°/7 mm.; *n*-$C_{12}H_{25}{\cdot}OH$ (95°; 10 hr.) gives p-*ethyl*-α-*methyl*-n-*undecylbenzene* (80%), b.p. 171—173°/7 mm. (*c*) C_6H_6 + P_2O_5 0·5 mol. at 75° : $Bu^\alpha OH$ (6 hr.) gives *p*-$C_6H_4(CHMeEt)_2$ (68%), b.p. 104°/10 mm.; *n*-$C_5H_{11}{\cdot}OH$ (9 hr.) gives *p*-$C_6H_4(CHMePr^\alpha)_2$ (40%), b.p. 127—128°/14 mm. Absence of *o*-compounds is proved by the narrow boiling range, constancy of *n* and *d*, and purity (fluorescein test) of the *p*-$C_6H_4(CO_2H)_2$ produced by $Na_2Cr_2O_7$–H_2SO_4; only C_6H_4MeEt contains appreciable amounts of *o*-compound. R. S. C.

Electrolysis of magnesium aryl bromides in ethyl ether : behaviour of short-lived aryl free radicals. W. V. Evans, R. Pearson, and D. Braithwaite (*J. Amer. Chem. Soc.*, 1941, **63**, 2574—2576).—Aryl radicals formed by electrolysis of MgPhBr, *p*-$C_6H_4Me{\cdot}MgBr$, or *p*-$C_6H_4Cl{\cdot}MgCl$ in Et_2O undergo little coupling, but in the main give $(CHAr)_2$ with some EtOH (both by interaction with the Et_2O) and much polymeride. However, MgPhBr gives also appreciable amounts of Ph_2 and $C_6H_4Ph_2$. $CH_2Ph{\cdot}MgBr$ resembles alkyl Grignard reagents, giving $(CH_2Ph)_2$. In absence of diffusion (transference cell), MgPhBr gives at the anode appreciable amounts of PhBr. R. S. C.

High mol. wt. hydrocarbons and hydrocarbon intermediates II. L. A. Mikeska and C. A. Cohen (*J. Org. Chem.*, 1941, **6**, 787—794; cf. A., 1938, ii, 355).—The alkylaromatics (**I**) are obtained by reduction of the appropriate ketones by a modific-

ation of Clemmensen's method or by the action of Grignard reagents on the latter with subsequent dehydration of the *tert.*-carbinol. Alkylhydroaromatics are prepared by hydrogenation (PtO_2) of (I). Thus are obtained: *Ph* n-*heneicosyl ketone* (II), m.p. 73—76° from behenyl chloride, C_6H_6, and $AlCl_3$; n-*docosylbenzene*, b.p. 245—247°, m.p. 42—44°, by reduction of (II); ε-*phenyl*-Δ^{ε}-n-*hexacosene*, b.p. 255—256°/6 mm., from (II) and $MgBu^{\alpha}Cl$ in Et_2O followed by $H_2C_2O_4$ at 180—200°, reduced to ε-*phenyl*-n-*hexacosane*, b.p. 245—255°/4 mm., m.p. 32—33°, and subsequently to ε-cyclo*hexyl*-n-*hexacosane*, b.p. 245—250°/2 mm., m.p. 30—31°; n-*docosyl*-cyclo*hexane*, m.p. 49—50°; $C_{10}H_7$ n-*heneicosyl ketone*, m.p. 67—69°; n-*docosylnaphthalene*, m.p. 56—58°; ε-*naphthyl*-Δ^{ε}-n-*hexacosene*, b.p. 245—265°/3 mm., and -n-*hexacosane*, m.p. 39—40°; $C_{10}H_7$ α-n-*butyl*-n-*nonadecyl ketone*, b.p. 280—300°/4 mm.; 2-n-*butyl*-n-*eicosylnaphthalene*, b.p. 270—290°/5 mm.; *tetrahydronaphthyl* n-*heneicosyl ketone*, m.p. 61—62°; n-*docosyltetrahydronaphthalene*, b.p. 265—275°/2 mm., m.p. 43—45°; ε-*tetrahydronaphthyl*-Δ^{ε}-n-*hexacosene*, b.p. 290—300°/3 mm., and -n-*hexacosane*, b.p. 275—285°/3 mm.; n-*docosyldecahydronaphthalene*, m.p. 53—54°; *diphenylyl* n-*heneicosyl ketone*, m.p. 109—110°; n-*docosyldiphenyl*, m.p. 82—84·5°; ε-*diphenylyl*-Δ^{ε}-n-*hexacosene*, b.p. 290—310°/4 mm., and -n-*hexacosane*, b.p. 290—300°/2 mm., m.p. 44—45°.

H. W.

Influence of restricted rotation on the absorption spectra of aryl-substituted aromatic hydrocarbons.—See A., 1942, I, 40.

Coupling action of the Grignard reagent. VII. Di-*o*-methylbenzyl chlorides. R. C. Fuson, J. J. Denton, and J. W. Kneisley (*J. Amer. Chem. Soc.*, 1941, **63**, 2652—2653; cf. A., 1938, II, 445).—2 : 4 : 6 : 1-$C_6H_2Me_3$·CH_2Cl and MgMeI give (2 : 4 : 6 : 1-$C_6H_2Me_3$·$CH_2)_2$ (86%), m.p. 117—117·5°, with a little 1 : 3 : 5 : 2-$C_6H_2Me_3Et$. CH_2O–HCl at 35° give 1 : 3 : 5-$C_6H_3Me_2Bu^{\gamma}$ and 2 : 6-*dimethyl*-4-tert.-*butylbenzyl chloride*, b.p. 124—125°/6 mm. (with *di*-2 : 6-*dimethyl*-4-tert.-*butylmethane*, m.p. 135°), reduced by Zn dust in 10% aq. NaOH to 5-tert.-*butylhemimellitol*, b.p. 114—115°/17 mm. [$(NO_2)_3$-derivative, m.p. 136—136·5°], and converted by MgMeI into *di*-2 : 6-*dimethyl*-4-tert.-*butylbenzyl* (85%), m.p. 216—217° (Br_2-derivative, m.p. 190—191°), and a little 2-*ethyl*-5-tert.-*butyl*-m-*xylene*, b.p. 125°/20 mm. [$(NO_2)_2$-derivative, m.p. 128·5—129°, obtained by fuming HNO_3 at <5°].

R. S. C.

Preparation and dehydrogenation of *spiro*decane and 3-methyl*spiro*decane. C. S. Marvel and L. A. Brooks (*J. Amer. Chem. Soc.*, 1941, **63**, 2630—2632).—*cyclo*Pentanone and CH_2:CH·$[CH_2]_3$·MgBr in Et_2O give 1-Δ^{δ}-n-*pentenyl*cyclo*pentanol* (53%), b.p. 82—83°/4 mm., 209—211°/760 mm., dehydrated by distillation with I to Δ^{δ}-n-*pentenyl*-Δ^{1}-cyclo*pentene* or Δ^{δ}-n-*pentenylidene*cyclo*pentane* (90%), b.p. 172—175°, which in 84% H_2SO_4 at 5—10° gives a mixture (*A*), b.p. 185—191° (rapidly forms peroxides), of the *spiro*decene $CH\text{—}CH_2$ ‖ $CH\cdot[CH_2]_3$ >C<$[CH_2]_4$, and the internal ether of 1-hydroxy-δ-hydroxy-n-amyl*cyclo*pentane. Hydrogenation (Raney Ni; 175°/1900 lb.) of (*A*) and washing the product with conc. H_2SO_4 and then oleum gives *spiro*decane, $[CH_2]_5$>C<$[CH_2]_4$, b.p. 184—186·5°, which does not react with Br or with Se at 300—350°, but with Pd–C at 290° gives 34·7% or with Pt–C at 320—325° gives 33·5% of $C_{10}H_8$. 3-Methyl*cyclo*pentanone gives similarly 1-Δ^{δ}-n-*pentenyl*cyclo*pentanol* (52%), b.p. 105—106°/12 mm., 214—217°/760 mm., a *diene*, b.p. 186—189°, impure methyl*spiro*decene, b.p. 198—203°, and *methyl*spiro*decane* (I), $[CH_2]_5$>C<$CH_2\cdot CH_2$ / $CH_2\cdot CHMe$, b.p. 195—197°. With Pd–C at 325° (not Se at 320—330°), (I) gives 31% of 2- but no 1-$C_{10}H_7Me$.

R. S. C.

Preparation of 2-bromonaphthalene. M. S. Newman and P. H. Wise (*J. Amer. Chem. Soc.*, 1941, **63**, 2847).—2-$C_{10}H_7$·N_2Cl with sufficient aq. $Hg(NO_3)_2$–NaBr to give $(C_{10}H_7$·$N_2Br)_2HgBr_2$ gives 53—59% of 2-$C_{10}H_7Br$, but with 2 equivs. gives 61—65%, further increase having no effect.

R. S. C.

Synthesis of 1-methyl-, 1-ethyl-, and 3-ethyl-4 : 5-methylenephenanthrene. W. E. Bachmann and J. C. Sheehan (*J. Amer. Chem. Soc.*, 1941, **63**, 2598—2600).—4 : 5-Methylenephenanthrene, Ac_2O, and $AlCl_3$ in $PhNO_2$ at −5° (later 0°) give 1- (30%), m.p. 152—153·5° (cf. Fieser *et al.*, A., 1940, II, 272), and 3-*acetyl*- (21%), m.p. 93·5—96·5°, reduced (Zn–Hg–HCl–AcOH–H_2O–PhMe) to 1- (I), m.p. 57·5—58·5° (*picrate*, m.p. 113—113·5°), and 3-*ethyl*-4 : 5-*methylenephenanthrene* (II), m.p. 86·5—87·5° (*picrate*, m.p. 109—110·5°), respectively. 1-Keto-4 : 5-methylene-1 : 2 : 3 : 4-tetrahydrophenanthrene with MgEtBr or MgMeI in boiling Et_2O gives carbinols, converted by Pd–C–N_2 at 280—300° into (I) and 1-*methyl*-4 : 5-*methylenephenanthrene*, m.p. 83·5—84·5° (*picrate*, m.p. 161·5—162·5°), respectively. 2-$C_{10}H_7Et$ with paraformaldehyde–conc. HCl–AcOH–H_3PO_4 gives 2 : 1-$C_{10}H_6Et$·CH_2Cl, b.p. 145—148°/5 mm., converted by boiling KCN–$COMe_2$–H_2O, followed by conc. HCl–AcOH, into 2-*ethyl*-1-*naphthylacetic acid* (III) (43%), m.p. 161·5—163°. Distillation of the Na salt of (III) with soda-lime gives 1 : 2-$C_{10}H_6$MeEt [picrate, m.p. 94—95° (lit. 97°)] (proof of structure), obtained also (picrate, m.p. 94·5—95·5°) from Me 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate by treatment with EtI–NaOMe–MeOH–C_6H_6, then HCl–AcOH–H_2O–N_2 (gives 1-keto-2-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 140—150°/10 mm.), and finally Pd–C–N_2 at 310°. The acid chloride ($SOCl_2$ and a little C_5H_5N in Et_2O) of (III) with $AlCl_3$ in C_6H_6 at room temp. gives 1-*ethyl*-7-*acenaphthenone* (85%), m.p. 68—69°, reduced by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ to 1-*ethyl*-7-*acenaphthenol* (86%), m.p. 117—118°. By the $CH_2(CO_2H)_2$ procedure (A., 1941, II, 91) this gives 1-*ethyl*-7-*acenaphthylacetic acid* (66%), m.p. 113—114°, and thence (Arndt–Eistert–Wolff; cyclisation by $SnCl_4$) 1-*keto*-6-*ethyl*-4 : 5-*methylene*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (60%), m.p. 108—109·5°. Clemmensen reduction and subsequent dehydrogenation by Pd–C then gives (II).

R. S. C.

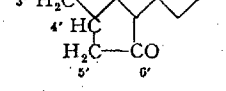
Preparation and chemistry of pyrene.—See B., 1941, II, 409.

Modification of the synthesis of 3 : 4-benzpyrene from pyrene. W. E. Bachmann, M. Carmack, and S. R. Safir (*J. Amer. Chem. Soc.*, 1941, **63**, 1682—1685).—γ-3-Pyrenyl-*n*-butyric acid (I) is prepared from the γ-CO-acid by Zn–Hg in AcOH–xylene–PhCl. In absence of AcOH a small amount of dilactone, m.p. 250—260°, is obtained, its structure following from fission by boiling KOH–EtOH to γ-hydroxy-γ-3-pyrenyl-*n*-butyric acid, which in hot xylene gives the lactone, m.p. 176—176·5°. Conversion of crude 4'-keto-1' : 2' : 3' : 4'-tetrahydro-3 : 4-benzpyrene into 3 : 4-benzpyrene, new m.p. 179—180° (corr.), is best (80%) effected by $Al(OPr^{\beta})_3$ and subsequent dehydration and dehydrogenation by Pd–C. 4'-*Hydroxy*-1' : 2' : 3' : 4'-*tetrahydro*-3 : 4-*benzpyrene* has m.p. 141·5—142° (corr.).

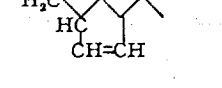
R. S. C.

5 : 4'-Dimethylene-3 : 4-benzpyrene. W. E. Bachmann and M. Carmack (*J. Amer. Chem. Soc.*, 1941, **63**, 1685—1688).—4'-Hydroxy-1' : 2' : 3' : 4'-tetrahydro-3 : 4-benzpyrene and HCl–C_6H_6 at room temp. give the 4'-*Cl*-compound (I) (94%), m.p. 150° (decomp.), which with $CHNa(CO_2Et)_2$ in boiling C_6H_6 gives an ester (and a little 1' : 2'-dihydro-3 : 4-benzpyrene), converted by hydrolysis and decarboxylation (190—200°) into 1' : 2' : 3' : 4'-*tetrahydro*-3 : 4-*benzpyrenyl*-4'-*acetic acid* (II), m.p. 194—195°. In boiling C_5H_5N, (I) gives the ? pyridinium salt and 1' : 2'-*dihydro*-3 : 4-*benzpyrene*, m.p. 149·5—150° [*picrate*, m.p. 170—180° (decomp.)], dehydrogenated by Pd–C at 320° to 3 : 4-benzpyrene. With PCl_5 and later $SnCl_4$ in C_6H_6 at room temp., (II) gives 6'-*keto*-5 : 4'-*dimethylene*-1' : 2' : 3' : 4'-*tetrahydro*-3 : 4-*benzpyrene* (III) (98%), m.p. 192—193° (vac.), which by successive reduction

(III.)



(IV.)

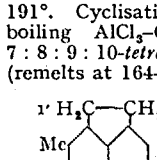


[$Al(OPr^{\beta})_3$–$Pr^{\beta}OH$] and dehydration (180°/1 mm.) gives the *hydrocarbon* (IV) (65%), m.p. 209—213° (*picrate*, m.p. 177·5—178°), dehydrogenated by Pd–C at 310—330° (N_2) to 5 : 4'-*dimethylene*-3 : 4-*benzpyrene* (V) (purified by adsorption on Al_2O_3), m.p. 251—252° (uncorr.), 255—256° (corr.) (*picrate*, m.p. 177—177·5°). 1-Ketotetrahydrocholanthrene gives similarly 1-*hydroxytetrahydrocholanthrene*, m.p. 150—150·5°, and thence cholanthrene. The absorption spectrum of (V) resembles that of 3 : 4-benzpyrene.

R. S. C.

Synthesis of 5-methyl-6 : 7-dimethylenechrysene and 1-methylcholanthrene. W. E. Bachmann and S. R. Safir (*J. Amer. Chem. Soc.*, 1941, **63**, 2601—2603).—1-Keto-11-methyl-1 : 2 : 3 : 4-tetrahydrochrysene and distilled $Al(OPr^{\beta})_3$ in

boiling Pr$^{\beta}$OH give the 1-*OH*-compound (82%), m.p. 149—150·5°, which affords (HCl–$CaCl_2$–C_6H_6 at 5°) the chloride, m.p. 132—133° (decomp.), and thence [NaOEt–$CH_2(CO_2Et)_2$–EtOH–C_6H_6, later 45% KOH at 100°] the malonic acid (77%), m.p. 177—178° (decomp.), and (heat at 200—210°) 11-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*chrysenylacetic acid* (78%), m.p. 190—191°. Cyclisation thereof by boiling PCl_5–C_6H_6, followed by boiling $AlCl_3$–CS_2, gives 1′-*keto*-5-*methyl*-6 : 7-*dimethylene*-7 : 8 : 9 : 10-*tetrahydrochrysene* (82%), m.p. 163—164° (vac.) (remelts at 164—164·5°), reduced (Zn–Hg–conc. HCl–AcOH–PhMe) to 5-*methyl*-6 : 7-*dimethylene*-7 : 8 : 9 : 10-*tetrahydrochrysene*, m.p. 105—113°, which with Pd–C at 310° gives 5-*methyl*-6 : 7-*dimethylenechrysene* (I) (44%), m.p. 167·5—168·3° (vac.) (remelts at 169—169·5°) (purified by adsorption of impurities on Al_2O_3). 1-Keto-2*a* : 3 : 4 : 5-tetrahydrocholanthrene and MgMeI in cold Et_2O give 1-hydroxy-1-methyl-2*a* : 3 : 4 : 5-tetrahydrocholanthrene, m.p. (crude) 60—70°, converted by Pd–C–N_2 at 300—320° into (probably 1-)*methylcholanthrene* (67%), m.p. 169—170° [*picrate*, m.p. 148·5—150° (vac.)]. R. S. C.



(I.)

Activation of aromatic halogen. R. Baltzly and J. S. Buck (*J. Amer. Chem. Soc.*, 1941, **63**, 1757).—Attempts to alkylate *p*-$C_6H_4Br{\cdot}NH_2$ etc. failed owing to reduction by HI (HI–red P gives 92% of NH_2Ph) or HBr (48% acid at 150° gives NH_2Ph and 2 : 4 : 1-$C_6H_3Br_2{\cdot}NH_2$). R. S. C.

Reductive alkylation of hindered aromatic amines. II. W. S. Emerson and E. L. Ringwald (*J. Amer. Chem. Soc.*, 1941, **63**, 2843—2844; cf. A., 1940, II, 339).—With Zn–Hg–CH_2O–AcOH–conc. HCl 2 : 6 : 4 : 1-$C_6H_2Br_2I{\cdot}NH_2$ gives 81% of $NPhMe_2$, but 4 : 6 : 1 : 3-$C_6H_2Cl_2(NH_2)_2$, m.p. 138—139° (lit. 136—137°), gives 4 : 6-*dichlorotetramethyl*-m-*phenylenediamine* (71%), m.p. 222—223°. R. S. C.

Rearrangement of *N*-triphenylmethyl-*o*-toluidine. Direct synthesis of 4-aminophenyl-3-methyltriphenylmethane. H. A. Iddles and A. S. Hussey (*J. Amer. Chem. Soc.*, 1941, **63**, 2768—2770).—*m*-$C_6H_4Me{\cdot}MgBr$ and $COPh_2$ in Et_2O give *m*-$C_6H_4Me{\cdot}CPh_2{\cdot}OH$, m.p. 54—55°, b.p. 204—206°/4—5 mm., reduced by Zn dust to *m*-$C_6H_4Me{\cdot}CHPh_2$ and converted by NH_2Ph,HCl in boiling AcOH into *p-aminotriphenyl*-m-*tolylmethane* (62%), m.p. 152° (Ac derivative, m.p. 189°), which, when diazotised by *n*-$C_5H_{11}{\cdot}O{\cdot}NO$–$H_2SO_4$–AcOH and then boiled with Zn dust in EtOH, gives *triphenyl*-m-*tolylmethane* (I), m.p. 161° [$(NO_2)_4$-derivative, m.p. 262°]. *o*-$C_6H_4Me{\cdot}NHBz$, BzCl, and $ZnCl_2$ at 220—230° give a product, hydrolysed to 2 : 1 : 5-$NH_2{\cdot}C_6H_3Me{\cdot}COPh$, which with MgPhBr and later Ac_2O–AcOH gives *diphenyl*-6-*acetamido*-m-*tolylcarbinol*, m.p. 166°. Reduction by Zn dust and AcOH then gives *diphenyl*-6-*acetamido*-p-*tolylmethane*, m.p. 150°, and condensation with NH_2Ph,HCl in AcOH gives *diphenyl*-6-*acetamido*-m-*tolyl*-4′-*aminophenylmethane*, m.p. 222—224° (6 : 4′-Ac_2 derivative, m.p. 267°), converted as above into *triphenyl*-6-*acetamido*-m-*tolylmethane*, m.p. 253°. Finally hydrolysis gives 2 : 1 : 5-$NH_2{\cdot}C_6H_3Me{\cdot}CPh_3$ (II), m.p. 215°, obtained also from *o*-$C_6H_4Me{\cdot}NH_2$ by $CPh_3{\cdot}OH$ in AcOH. Diazotisation of (II) and elimination of NH_2 as above gives (I), but decomp. of the diazonium sulphate in boiling H_2O gives the OH-derivative, m.p. 183°, and thence the OEt-derivative, m.p. 144·5°. These results confirm the views previously reported (A., 1941, II, 10). R. S. C.

Phenylacet-*n*-butylamide, m.p. 57°.—See A., 1942, I, 106.

Di-aryl- and -*cyclo*alkyl-ethanolamines. J. B. Niederl and R. Lay (*J. Amer. Chem. Soc.*, 1941, **63**, 1498—1499).—$NH_2{\cdot}CH_2{\cdot}CO_2Et$,HCl (1 mol.) and MgRHal (10 mols.) in boiling Et_2O give *β-hydroxy-ββ-di*-o-*anisyl*-, m.p. 115° [*hydrochloride*, m.p. 199°; *picrate*, m.p. 197° (decomp.)], -p-*anisyl*-, m.p. 112° [*hydrochloride*, m.p. 148°; *picrate*, m.p. 159° (decomp.); *phenylthiocarbamide*, m.p. 158°; N-*Bz* derivative, m.p. 118°], -p-*phenetyl*-, m.p. 80° [*hydrochloride*, m.p. 127°; *picrate*, m.p. 135° (decomp.)], -o-, m.p. 152° [*hydrochloride*, m.p. 247° (decomp.); *picrate*, m.p. 219° (decomp.)], -m-, m.p. 79° [*hydrochloride*, m.p. 175°; *picrate*, m.p. 185° (decomp.)], and -p-*tolyl*-, m.p. 125° [*hydrochloride*, m.p. 195°; *picrate*, m.p. 186° (decomp.)], -p-*phenoxyphenyl*-, m.p. 135° [*hydrochloride*, m.p. 149° (decomp.); *picrate*, m.p. 163° (decomp.)], and -cyclo*hexyl*-, m.p. 101° [*hydrochloride*, m.p. 202°; *picrate*, m.p. 154° (decomp.)], -*ethylamine*. R. S. C.

Synthesis of some iodinated aromatic compounds. L. Long, jun. and A. Burger (*J. Amer. Chem. Soc.*, 1941, **63**, 1586—1589).—2 : 4 : 6 : 1-$C_6H_2I_3{\cdot}NH_2$ does not react with *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ (I), CH_2O–KCN, $CH_2I{\cdot}CO_2Et$, $CH_2I{\cdot}CO_2Et$–C_5H_5N–PhCl, $NH_2{\cdot}CO{\cdot}NH{\cdot}NO_2$ (II), or Ac_2O, but with Ac_2O and a drop of H_2SO_4 gives the *Ac* derivative, m.p. 276—277° (decomp.). 2 : 4 : 1-$C_6H_3I_2{\cdot}NH_2$ (III) with (I) in C_5H_5N gives N^1-2′ : 4′-*di-iodophenylsulphanilamide*, m.p. 176—178° (by way of the N^4-*Ac* derivative, m.p. 230—231°), and with CH_2O–KCN–KOH–EtOH–H_2O (2%) or $CH_2I{\cdot}CO_2Et$–C_5H_5N (later KOH–EtOH) (4·2%) gives 2 : 4-*di-iodophenylglycine*, m.p. 161—162° (decomp.), better (28%) obtained from $NHPh{\cdot}CH_2{\cdot}CO_2H$ by KI–KIO_3–conc. HCl–EtOH. In C_5H_5N–EtOH (not EtOH) at room temp., (II) and (III) give 2 : 4-*di-iodophenylcarbamide* (29%), m.p. 294—295° (decomp.), and a *substance*, m.p. 188—189°. 2 : 4 : 6 : 1-$C_6H_2I_3{\cdot}OH$ (*chloroacetate*, m.p. 141—142°) with NaOBu–$CH_2Cl{\cdot}CO_2Et$–BuOH or $CH_2I{\cdot}CO_2Et$–EtOH gives 2 : 4 : 6 : 1-*tri-iodophenoxyacetic acid* (74%), m.p. 224—225° (decomp.) (*Na* salt); the Na phenoxide with the appropriate Cl-amine in abs. EtOH gives *β*-2 : 4 : 6-*tri-iodophenoxyethyl*-, m.p. 195—196° (decomp.) [corresponding *picrate*, m.p. 146—148° (decomp.)], *γ*-2 : 4 : 6-*tri-iodophenoxy*-n-*amyl*-, m.p. 190° (decomp.), and -n-*hexyl-diethylamine hydrochloride*, m.p. 188—190° (decomp.) [and another hydrochloride, m.p. 160—170° (decomp.)]. R. S. C.

δ-Substituted semicarbazides. I. Synthesis of some derivatives. R. Barré and L. Piché (*Canad. J. Res.*, 1941, **19, B**, 158—171).—δ-p-*Nitrophenylsemicarbazide*, m.p. 191° (decomp.) [*hydrochloride*, m.p. 265° (block)], is obtained by condensation of *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH_2$ with N_2H_4,H_2O in boiling aq. EtOH (method *A*), by treatment of *p*-$NO_2{\cdot}C_6H_4{\cdot}NCO$ with N_2H_4,AcOH in light petroleum–$COMe_2$, and (method *B*) by interaction of *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ with $NH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CMe_2$ in boiling xylene. It gives *acetone*-, m.p. 264° (decomp.), and *glucose*-, m.p. 192—193°, -δ-p-*nitrophenylsemicarbazone*. δ-p-*Nitrobenzylsemicarbazide*, m.p. 164° [*hydrochloride*, m.p. 195—197° (decomp.)], obtained by method *B*, affords *acetone*-, m.p. 162°, and (impure) *glucose*-δ-p-*nitrobenzylsemicarbazone*. δ-p-*Nitroxenylsemicarbazide*, m.p. 178° (obtained by method *B*), its *hydrochloride*, m.p. 219°, *acetone*-, m.p. 261°, and *glucose*-, m.p. 172°, -δ-p-*nitroxenylsemicarbazone* are described. δ-2 : 4-*Dinitrophenylsemicarbazide*, m.p. 178°, obtained by method *A* (*acetone*-δ-2 : 4-*dinitrophenylsemicarbazone*, m.p. 248°), yields ill-defined derivatives with glucose. The mechanism of all these reactions consists in the elimination of NH_2 of the amine as NH_3 and union of the aryl or alkyl residue with the amide. The theory of the rearrangement of $CO(NH_2)_2$ into NH_4NCO and the isomerisation of substituted carbamides to the corresponding carbimides is inadequate to interpret many of the observed phenomena and is in conflict with the observed yields. It is not applicable to the synthesis of semicarbazides. H. W.

Synthesis of dialkylaminoalkyl arylthiourethanes and thiocarbamides. T. F. Wood and J. H. Gardner (*J. Amer. Chem. Soc.*, 1941, **63**, 2741—2742).—$NH_2{\cdot}[CH_2]_{2-3}{\cdot}OH$ and RCNS in xylene give *β*-diethylaminoethyl phenyl-, an oil (*hydrochloride*, m.p. 121—122°), and *p*-dimethylaminophenyl-thiourethane, m.p. 76° [*hydrochloride*, m.p. 162—163° (decomp.)], and *γ*-diethylamino-*n*-propyl phenylthiourethane, m.p. 76—77° [*hydrochloride*, m.p. 98—100° (decomp.)]. *β*-Morpholinoethylamine and RCNS in C_6H_6 give *N*-*β*-morpholinoethyl-*N*′-phenyl-, m.p. 109° (*hydrochloride*, m.p. 156—156·5°), and -*p*-dimethylaminophenyl-thiocarbamide, m.p. 97° (*hydrochloride*, m.p. 166°). The thiourethanes have local anæsthetic, but no hypnotic or analgesic, action, but the thiocarbamides are ineffective. R. S. C.

The azo-group as a chelating group. V. Metallic derivatives of arylazo-oximes and of formazyl compounds. L. Hunter and C. B. Roberts (*J.C.S.*, 1942, 823—826; cf. A., 1940, II, 251).—Piperonalphenylhydrazone and $C_5H_{11}{\cdot}NO_2$–Na–EtOH afford *benzeneazopiperonaldoxime* (I), m.p. 138° (decomp.), and nitrosation of *p*-tolualdehydephenylhydrazone similarly gives *benzeneazo*-p-*tolualdoxime* (II), m.p. 133° (decomp.), or of benzaldehyde-*p*-tolylhydrazone, p-*tolueneazobenzaldoxime* (III), m.p. 111° (decomp.). Benzeneazo-acetaldoxime, -benzaldoxime, -anisaldoxime, (II), (I), or (III) with aq. $Co(OAc)_2$–EtOH affords the respective *Co*^{III} *complexes*, m.p. 238° (decomp.), 133°, 210° (decomp.), 149°, 145°,

and 145°, respectively. Diphenyl- (**IV**), phenyl-*p*-tolyl- (**V**), -*p*-anisyl- (**VI**), -*p*-bromophenyl- (**VII**), or -α- or -β-naphthylformazylbenzene with aq. $Ni(OAc)_2$–EtOH affords *Ni complexes*, m.p. 300° (decomp.), 287° (decomp.), 273° (decomp.), 278° (decomp.), 262° (decomp.), and 277°, respectively; with aq. $Co(OAc)_2$–EtOH, the same compounds yield *Co*^{II} *compounds*, m.p. 228—230°, 238°, 233° (decomp.), 192° (decomp.), 190° (decomp.), and 186° (decomp.), respectively, and (**IV**), (**V**), (**VI**), and (**VII**) with $Cu(OAc)_2$–EtOH–$COMe_2$ afford *Cu*^{II} *complexes*, m.p. 158°, 156°, 163°, and 140°, respectively. Formulæ for the Co and Ni complexes are suggested.

A. T. P.

Associating effect of the hydrogen atom. IX. N–H–N bond. Virtual tautomerism of the formazyl compounds. L. Hunter and C. B. Roberts (*J.C.S.*, 1941, 820—823).—Three pairs of alleged isomerides (phenyl-α- and -β-naphthyl- and -*p*-bromophenyl-formazylbenzene) are shown to be three individuals and from physical properties and the isolation of chelate metallic derivatives, the formazyl compounds are regarded as resonance hybrids of *a* and *b*.

F. R. S.

Relation between absorption spectra and chemical constitution of dyes. XVI. Separation of chromophores in unsymmetrical bisazo-dyes. W. R. Brode and J. D. Piper (*J. Amer. Chem. Soc.*, 1941, **63**, 1502—1505; cf. A., 1940, II, 165).—Pure *as*-bisazo-dyes are prepared from diamines by successive monoacetylation (Ac_2O in much EtOH), diazotisation, coupling with $NPhMe_2$ in dil. AcOH (2—14 days), hydrolysis in EtOH, diazotisation, and coupling with *p*-cresol. Thus are obtained 4-*amino*-4′-*acetamido-diphenylmethane*, m.p. 121—122°, -*dibenzyl*, m.p. 141—147°, and -*stilbene*, m.p. 238—238·5°, *p*-NMe_2·C_6H_4·N_2Ph, m.p. 191—191·3° (lit. 186—187°) [Ac derivative, m.p. 227—227·5° (lit. 217°)], 4-*amino*-4′-*dimethylamino-diphenyl*, m.p. 226—227° (*Ac* derivative, m.p. 278—281°), -*diphenylmethane*, m.p. 132—139 (*Ac* derivative, m.p. 158—159°), -*dibenzyl*, m.p. 242—246° (*Ac* derivative, m.p. 248—249°), and -*stilbene*, m.p. 242—246° (*Ac* derivative, m.p. 282—285°), p-p′-*dimethylaminobenzeneazo*-2″-*hydroxy*-5″-*methylbenzeneazobenzene*, m.p. 185—186°, 4-p-*dimethylaminobenzeneazo*-4′-2″-*hydroxy*-5″-*methylbenzeneazo-diphenyl*, m.p. 219·5—220°, -*diphenylmethane*, m.p. 166—167°, -*dibenzyl*, m.p. 199·5—200·5°, and -*stilbene*, m.p. 251—254°. Absorption spectra of these dyes in EtOH, 3% NaOH, dil. and conc. HCl are recorded and compared with those of 2 : 5 : 1-OH·C_6H_3Me·N_2Ph and *p*-NMe_2·C_6H_4·N_2Ph. CH_2 or $[CH_2]_2$ insulates the resonators, CH:CH couples them into a single resonator, and union to C_6H_4·C_6H_4 represses the absorption band (cf. *s*-bisazo-dyes, A., 1935, 335). R. S. C.

Diazotisation. J. Kenner (*Chem. and Ind.*, 1941, 899).—Polemical (cf. Earle and Hills, A., 1942, II, 52). A. T. P.

1-α-Naphthyl*cyclo*hexan-1-ol. R. D. Kleene (*J. Amer. Chem. Soc.*, 1941, **63**, 1768).—1-α-Naphthyl*cyclo*hexan-1-ol, m.p. 66—68°, is obtained in 40% yield from 1-$C_{10}H_7$·MgBr and *cyclo*hexanone in Et_2O. R. S. C.

Action of formaldehyde on *o*-chlorophenol and 2 : 4-dichlorophenol.—See 1942, II, 112.

Configuration of synthetic œstrogenic substances. F. von Wessely and H. Welleba (*Naturwiss.*, 1940, **28**, 780).—γδ-Di-*p*-hydroxyphenylhexane (cf. Dodds *et al.*, A., 1939, II, 312) with α-bromo-π-camphorsulphonic acid gives optical isomerides, m.p. 80·5°, $[\alpha]_D$ (+) +17·7°, (−) −17·6°, in EtOH, the (+)-isomeride having the more potent œstrogenic action. Catalytic hydrogenation of *cis*- and *trans*-dimethylstilbene occurs approx. quantitatively in *cis*-positions. Diethylstilbœstrol and its Me_2 ether are reduced smoothly to *dl*-forms. J. L. D.

Blocking effects in condensation reactions. J. B. Niederl and J. S. McCoy (*J. Amer. Chem. Soc.*, 1941, **63**, 1731—1733; cf. A., 1937, II, 336; 1940, II, 371).—MeCHO or PhCHO (1 mol.) with *m*-2- or *m*-4-xylenol (1 or 2 mols.) in AcOH–HCl at 0° gives 4 : 4′-, m.p. 131° (*diacetate*, m.p. 148°), and 2 : 2′-*dihydroxy*-3 : 5 : 3′ : 5′-*tetramethyltriphenylmethane*, m.p. 163° (*diacetate*, m.p. 155°), α*a*-*di*-4- m.p. 143° (*diacetate*, m.p. 111°), and -2-*hydroxy*-3 : 5-*dimethylphenylethane*, m.p. 133°. By addition of HCl and condensation, CHMe:CH·CHO gives γ-*chloro*-α*a*-*di*-4-, m.p. 199° (*diacetate*, m.p. 108°), and -2-*hydroxy*-3 : 5-*dimethylphenyl*-n-*butane*, m.p. 152°.

R. S. C.

Oxidation products of $\Delta^{9:10}$-octahydronaphthalene. W. P. Campbell and G. C. Harris (*J. Amer. Chem. Soc.*, 1941, **63**, 2721—2726).—$\Delta^{9:10}$-Octahydronaphthalene (**I**) (prep. in 78% yield from decahydro-β-naphthol by P_2O_5–85% H_3PO_4 at 150° and later P_2O_5 at 140°), b.p. 190—192° (nitrosochloride, m.p. 92·5°), and SeO_2 (0·5 mol.) in Ac_2O at 3→5° give $\Delta^{9:10}$-*octahydronaphthyl acetate* (**II**) (65%), b.p. 125—127°/10 mm., hydrolysed by boiling 2% NaOEt–EtOH to the alcohol, which with $Al(OBu^{\gamma})_3$–$COMe_2$–C_6H_6 at 75—80° gives 1-keto-$\Delta^{9:9}$-octahydronaphthalene (**III**) (65%), b.p. 127—128°/10 mm. (oxime, m.p. 146—147°; semicarbazone, m.p. 241—242°) (cf. Hückel *et al.*, A., 1933, 704). The structure of (**III**) follows from its absorption spectrum [max. at 243 (log *E* 4·0) and 305 mμ. (log *E* 1·8)], but it could not be resolved by way of the *l*-menthylhydrazone (prep. from *l*-menthyl *N*-aminocarbamate), m.p. 166·5—167°, $[\alpha]_D^{25}$ −203° in $CHCl_3$. $(CH_2{:}CMe)_2$ does not condense with (**III**) at 100°. With SeO_2 (1 mol.) in Ac_2O at 25—30°, (**I**) gives (**II**) (35%) and the *diacetate* (12·5%), m.p. 122—123°, b.p. 145—148°/2 mm., hydrolysed by alcoholic alkali to 1 : 5-*dihydroxy*-$\Delta^{9:10}$-*octahydronaphthalene* (**V**), m.p. 195·5—197°; similar oxidation of (**II**) gives 16% of (**IV**). Oppenauer oxidation of (**V**) gives $\Delta^{9:10}$-*octahydronaphthalene*-1 : 5-*dione* (**VI**) (30%), m.p. 113—114° [*dioxime*, m.p. >285°; absorption max. at 263 mμ. (log *E* 4·1)], converted by Pd–C at 330° into 1 : 5-$C_{10}H_6(OH)_2$ (isolated as diacetate). With SeO_2 (1 mol.) in Ac_2O at 120—124°, (**I**) gives a *diacetate* (**VII**), m.p. 139—140° [and some (**II**)], hydrolysed to 1 : 5-*dihydroxy*-1 : 2 : 3 : 5 : 6 : 7-*hexahydronaphthalene*, m.p. 155·5—156·5° [absorption max. at 238 mμ. (log *E* 4·2)], which is oxidised (Oppenauer) to (**VI**) and does not react with NH_2OH or hot 2% NaOH–EtOH. At 70°, SeO_2 gives a mixture of (**II**), (**IV**), and (**VI**). Hydrogenation (PtO_2) of (**IV**) in AcOH gives 1 : 5-*dihydroxydecahydronaphthalene* (16%), m.p. 178—178·5°. R. S. C.

Reduction of the *o*-nitrophenyl esters of certain acids.—See A., 1942, II, 119.

Phenaeyl, *p*-phenyl- and *p*-bromo-phenacyl, and *p*-nitrobenzyl esters of α-hydroxy-fatty acids.—See A., 1942, II, 74.

Organic reactions with boron fluoride. XXIV. Cleavage reactions of benzyl *n*-propyl ether with boron fluoride. W. J. Monacelli and G. F. Hennion (*J. Amer. Chem. Soc.*, 1941, **63**, 1722—1724; cf. A., 1940, II, 270).—Cleavage of CH_2Ph·$COPr^{\alpha}$ (prep. described), b.p. 68°/8 mm., by BF_3 (0·45—0·5 mol.) in presence of AcOH or Ac_2O gives $Pr^{\alpha}OAc$ (58—64%) and a polymeride (derived from CH_2Ph^+), in presence of C_6H_6 gives CH_2Ph_2 and $C_6H_4(CH_2Ph)_2$ (with 1 mol. of BF_3 some $PhPr^{\beta}$ is also formed), in presence of $C_{10}H_8$ gives 1-$C_{10}H_7$·CH_2Ph (75%), in presence of PhOH gives *p*-CH_2Ph·C_6H_4·OH (47·7%), and in presence of C_6H_6 + AcOH or C_6H_6 + Ac_2O gives $Pr^{\alpha}OAc$ (50—64·7%), CH_2Ph_2, and $C_6H_4(CH_2Ph)_2$. The reaction mechanism probably involves fission into CH_2Ph^+ and $(Pr^{\alpha}O–BF_3)^-$. R. S. C.

2 : 4 : 5 : 6-Tetrachloro-*m*-anisidine and some derivatives. E. Bureš and I. Kárová (*Časop. Československ. Lék.*, 1938, **18**, 1—7).—2 : 4 : 5 : 6-*Tetrachloroacet*-m-*anisidide*, m.p. 181·5°, produced by chlorination of acet-*m*-anisidide (m.p. 80—81°) in Ac_2O, is hydrolysed to 2 : 4 : 5 : 6-*tetrachloro*-m-*anisidine* (**I**), m.p. 56·5° (*hydrochloride*; *Ac*$_2$, m.p. 65°, *Bz*, m.p. 153°, NN-*Me*$_2$, and N-*Et* derivatives). (**I**) could not be diazotised.

F. R.

Enediols. VI. Stilbenediols from duril and *iso*duril. R. C. Fuson and S. C. Kelton, jun. **VII. Bromostilbenediols.** R. C. Fuson, S. L. Scott, and R. V. Lindsey, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 1500—1502, 1679—1682; cf. A., 1941, II, 223).—VI. 2 : 3 : 5 : 6 : 1- and 2 : 3 : 4 : 6 : 1-C_6HMe_4·MgBr give, by the entrainment method, the C_6HMe_4·CO_2H, m.p. 179—180° and 164—166°, respectively, which with $SOCl_2$ give the acid chlorides, (**I**), m.p. 59—60°, b.p. 105—106°/6 mm., and (**II**), b.p. 102—103°/3 mm., respectively. With Mg + MgI_2–N_2, (**I**) gives *duril* (**III**), m.p. 250—251°, and cis-α*β*-*dihydroxy*-α*β*-*didurylethylene* (**IV**), m.p. 167—169° (N_2); (**II**) gives *iso*duril (**V**), m.p. 184—185°, but the diol could not be isolated. Hydrogenation of (**V**) in AcOH gives cis-α*β*-*dihydroxy*-α*β*-*diisodurylethylene* (**VI**), m.p. 142—144° (N_2), but in low-boiling light petroleum the product rearranges to *isoduroin*, m.p. 117—118° (*acetate*, m.p. 127—129°). Hydrogenation of (**III**) or (**V**) in MeOH gives

trans-*αβ-dihydroxy-αβ-di-duryl-* (**VII**), m.p. 214—215° (N_2), and -iso*duryl-ethylene* (**VIII**), m.p. 183—185° (N_2). HCl–MeOH rearranges (**VII**) to *duroin* (**IX**), m.p. 130—131° (*acetate*, m.p. 144—145°). With boiling Ac_2O–N_2, (**IV**) and (**VII**) give the cis- (**X**), m.p. 219—220°, and trans-$(OAc)_2$-compounds, m.p. 263—265°, respectively, but (**VI**) and (**VIII**) both give the trans-$(OAc)_2$-compound, m.p. 252—254°. cis-*αβ-Diacetoxy-αβ-di*iso*durylethylene*, m.p. 161—163°, and (**X**) are obtained by hydrogenating (**V**) and (**III**), respectively, in Ac_2O. With H_2–Cu chromite at 230°/5500 lb., (**III**) and (**V**) give *αβ-di-duryl-*, m.p. 235—236°, and -iso*duryl-ethylene*, m.p. 169—171°, respectively. With H_2–Raney Ni at 150°/2600 lb., (**III**) gives (**IV**). M.p. are corr.

VII. 4-*Bromo*-2 : 6-*dimethylbenzonitrile* (prep. from the amine), m.p. 71—72°, is readily hydrolysed by 70% H_2SO_4 at 170—180° to 4-*bromo*-2 : 6-*dimethylbenzoic acid*, m.p. 197—198°, the acid chloride ($SOCl_2$), m.p. 56—57°, of which with Mg + MgI_2 gives 4 : 4′-*dibromo*-2 : 6 : 2′ : 6′-*tetramethylbenzil* (**XI**), m.p. 211·5—212·5° (*oxime*, m.p. 222—223°), and *-benzoin* (**XII**), m.p. 143—144° [*acetate*, m.p. 163—164°; oxidised by $CuSO_4$–C_5H_5N–H_2O to (**XI**)]. Hydrogenation (PtO_2) of (**XI**) in MeOH or MeOH containing a drop of piperidine gives cis-, m.p. 124—125° [*diacetate*, m.p. 186·5—187·5°; rearranged to (**II**) by HCl–MeOH], and trans-4 : 4′-*dibromo*-2 : 6 : 2′ : 6′-*tetramethylstilbene-αβ-diol*, m.p. 183—184° (*diacetate*, m.p. 241—242°; *dibenzoate*, m.p. 265—267°), respectively, both very unstable in air. (2 : 4 : 6 : 1-$C_6H_2Me_3$·CO)$_2$ and Br–CCl_4–Fe powder give 3 : 3′-*dibromo*-2 : 4 : 6 : 2′ : 4′ : 6′-*hexamethylbenzil*, m.p. 181·5—182·5° (corr.), which with Na_2O_2 gives 2 : 4 : 6 : 3 : 1-C_6HMe_3Br·CO_2H, with H_2–PtO_2 in C_6H_6–light petroleum gives cis- (**XIII**), m.p. 158—160° (corr.; N_2), or by prolonged hydrogenation trans-3 : 3′-*dibromo*-2 : 4 : 6 : 2′ : 4′ : 6′-*hexamethylstilbene-αβ-diol*, m.p. 204·5—205·5° [*diacetate*, m.p. 237·5—239° (corr.)], and with H_2–PtO_2 in Ac_2O gives the *diacetate*, m.p. 197—198° (corr.), of (**XIII**). 3 : 3′-*Dibromo*-2 : 4 : 6 : 2′ : 4′ : 6′-*hexamethylbenzoin* has m.p. 133·5—135° (corr.). 3 : 3′-*Dibromo*-2 : 4 : 6 : 2′ : 4′ : 6′-*hexaethylbenzil* (**XIV**) (prep. as above), m.p. 113—114° (corr.), with Mg + MgI_2 gives cis- (**XV**), m.p. 138—139° (corr.; N_2) [*dibenzoate*, m.p. 210—211° (corr.), obtained by BzCl], and by prolonged hydrogenation gives trans-3 : 3′-*dibromo*-2 : 4 : 6 : 2′ : 4′ : 6′-*hexaethylstilbene-αβ-diol*, m.p. 179·5—180·5° (corr.; N_2) [*diacetate*, m.p. 211·5—212·5° (corr.)], and by hydrogenation in Ac_2O gives the *diacetate*, m.p. 152—152·7° (corr.), of (**XV**). Br–CCl_4–Fe powder and (**XIV**) give 3 : 5 : 3′ : 5′-*tetrabromo*-2 : 4 : 6 : 2′ : 4′ : 6′-*hexaethylbenzil*, m.p. 207·5—208° (corr.). The *m*-Br-enediols are stable in air. R. S. C.

Enediols. VIII. Methoxystilbenediols. R. C. Fuson, J. Corse, and P. B. Welldon. **IX. Enediols in the naphthalene series.** R. C. Fuson, C. H. McKeever, and L. C. Behr (*J. Amer. Chem. Soc.*, 1941, **63**, 2645—2648, 2648—2649; cf. preceding abstract).—VIII. Substitution by OMe does not affect the properties of stilbenediols. 2 : 4 : 6 : I-$C_6H_2Me_3$·OH gives 87% of 2-*bromo*-4-*methoxymesitylene*, m.p. 8°, b.p. 132—135°/17 mm., which affords (Grignard) 3-*methoxymesitoic acid* (43%), m.p. 104·5—105·5° (*amide*, m.p. 169°). The acid chloride, b.p. 138—139°/15 mm., thereof with Mg + MgI_2 gives 55% of cis-3 : 3′-*dimethoxy*-2 : 4 : 6 : 2′ : 4′ : 6′-*hexamethylstilbene-αβ-diol* (**I**), m.p. 138·5—139·5° (N_2), 26% of 3 : 3′-*dimethoxydimesityl* (**II**), m.p. 78—79, and, in two experiments, a small amount of (3 : 2 : 4 : 6 : 1-OMe·C_6HMe_3·C:)$_2$. Hydrogenation (PtO_2) of (**II**) in MeOH containing a trace of piperidine gives the trans-*diol* (**III**), m.p. 232—233° (N_2) (*diacetate*, m.p. 192—193° prepared by Ac_2O). Hydrogenation of (**II**) in Ac_2O gives the *diacetate*, m.p. 134—135°, of (**I**). Atm. oxidation of (**I**) is appreciable in 20 min., that of (**II**) inappreciable in 2 weeks. Neither (**I**) nor (**II**) ketonises spontaneously. 2 : 4 : 6 : 1-OMe·$C_6H_2Me_2$·COMe with NaOCl–H_2O–C_5H_5N gives 3 : 5-*dichloro*-6-*methoxy*-2 : 4-*dimethylbenzoic acid*, m.p. 120—121°. Na *s-m*-xylenoxide and CO_2 at 110° give only 10% of 6 : 2 : 4 : 1-OH·$C_6H_2Me_2$·CO_2H, m.p. 164—165° (Me ether, m.p. 166·5—167°). 1 : 3 : 2 : 5-$C_6H_2Me_2Br$·OH (prep. described), m.p. 112—114°, gives (Me_2SO_4–aq. NaOH) the Me ether, b.p. 131—134°/14—15 mm., the Grignard reagent from which yields 4-*methoxy*-2 : 6-*dimethylbenzoic acid*, m.p. 144·5—145°. The derived acid chloride ($SOCl_2$) with Mg + MgI_2 gives 2 : 6 : 2′ : 6′-*tetramethyl*-p-*anisil* (38%), m.p. 197—198·5°, the enediol from which exists (dichlorobenzeneindophenol test) but is too readily oxidised to be isolated.

IX. Stilbenediols containing 2 : 1-$C_{10}H_6Me$ are similar to those containing mesityl etc. 2-$C_{10}H_7Me$ and Br–CS_2 give 2 : 1-$C_{10}H_6MeBr$ (92%), b.p. 125—129°/5 mm., and thence (Grignard) 2 : 1-$C_{10}H_6Me$·CO_2H (**IV**) (72%), m.p. 124—126°, or (CuCN–C_5H_5N; 200—220°) 2-*methyl*-1-*naphthonitrile*, m.p. 87—88° (hydrolysed only to the amide). The acid chloride ($SOCl_2$) of (**IV**) with Mg + MgI_2 in C_6H_6–Et_2O–N_2 gives cis-*αβ-dihydroxy-αβ-di*-2-*methyl*-1-*naphthylethylene* (**V**), m.p. 186—188° (*diacetate*, m.p. 198—199°), and *di*-2-*methyl*-1-*naphthyl diketone* (**VI**), m.p. 160—160·5°. In MeOH, hydrogenation of (**VI**) gives (**V**) but in light petroleum gives the *trans*-isomeride (**VII**), m.p. not sharp (*diacetate*, m.p. 267—270°). HCl–MeOH converts (**VII**) into 2 : 2′-*dimethyl*-1 : 1′-*naphthoin*, m.p. 149—151·5°. Relative stabilities of (CR·OH)$_2$ are R = $C_6H_2Pr^{\beta}_3$ > $C_6H_2Et_3$ = 2 : 1-$C_{10}H_6Me$ > $C_6H_2Me_3$. M.p. are corr. R. S. C.

Vinyl alcohols. II. αβ-Dimesityl-Δ$^{\alpha}$-propen-α-ol. R. C. Fuson, D. J. Byers, and N. Rabjohn. **III. αβ-Diaryl-Δ$^{\alpha}$-propen-α-ols.** R. C. Fuson and C. A. Sperati (*J. Amer. Chem. Soc.*, 1941, **63**, 2639—2642, 2643—2644).—**II.** αβ-Dimesityl-Δ$^{\alpha}$-propen-α-ol (**I**) (A., 1941, II, 222) is insol. in conc. aq. or Claisen's alkali, gives no $FeCl_3$ colour and a doubtful Folin reaction, does not couple with ArN_2Cl or react with CH_2Cl·CO_2H, but with Me_2SO_4–KOH–MeOH gives *α-methoxy-αβ-dimesityl-Δ$^{\alpha}$-propene* (**II**) (42%), m.p. 185—186°. The mol. wts. of (**I**), its acetate, and (**II**) in boiling $CHCl_3$ are normal. It slowly liquifies when kept, giving in one experiment a trace of a *? peroxide*, m.p. 103—104°, but usually 2 : 4 : 6 : 1-$C_6H_2Me_3$·COMe + -$C_6H_2Me_3$·CO_2H, which are also formed in attempts to prepare the peroxide by O_2 in Et_2O–light petroleum or by ozonisation of (**I**) or its acetate in $CHCl_3$. $KMnO_4$, CrO_3, or bromanil dehydrogenates (**I**) to mesityl α-mesitylvinyl ketone (prep. from deoxymesitoin modified to give 87% yield). Ketonisation of (**I**) was effected only by boiling HCl–MeOH, thus giving *α-mesitylpropiomesitylene* (**III**), m.p. 73·5—74·5°, whence it is regenerated by boiling NaOEt–EtOH. Boiling syrupy H_3PO_4 hydrolyses (**III**) to *s*-$C_6H_3Me_2$ and *α-mesitylpropionic acid*, m.p. 104—105°.

III. Four analogues closely resemble (**I**). The stability is the greater the higher is the m.p. 1 : 2 : 3 : 5-$C_6H_2Me_4$ and CH_2O–HCl give 2 : 3 : 4 : 6-*tetramethylbenzyl chloride* (50%), b.p. 113—115°/5 mm., and thence iso*durylacetonitrile* (74%), m.p. 74—75°, b.p. 134—135°/5 mm. The following are prepared by the author's methods, acetates by Ac_2O. *Mesitylaceto-durene*, m.p. 118·5—119·5°, and -iso*durene*, m.p. 99·5—100·5°. iso*Duryl-*, m.p. 98·5—100°, and *duryl-acetomesitylene*, m.p. 113—114°, b.p. 198—203°/2—3 mm. *Duryl*, m.p. 159—160°, and iso*duryl α-mesitylvinyl ketone*, m.p. 140·5—141°. *Mesityl* α-iso*duryl-*, m.p. 142—142·5°, and *α-durylvinyl ketone*, m.p. 166·5—167·5°. *β-Mesityl-α-duryl-* (**IV**), m.p. 136—136·5° (*acetate*, m.p. 124·5—125°), *β-mesityl-α-iso-duryl-* (**V**), m.p. (+EtOH) 63—64° and (solvent-free) 73—74° (*acetate*, m.p. 128·5°), *α-mesityl-β-*iso*duryl-*, m.p. 96—97° (*acetate*, m.p. 125·5—126·5°), and *α-mesityl-β-duryl-*, m.p. 144·5—145·5° (*acetate*, m.p. 147—148°), *-Δ$^{\alpha}$-propen-α-ol.* iso*Duryl-*, m.p. 167—168° (*amide*, m.p. 229·5—230°), and *duryl-acetic acid*, m.p. 204·5—205° (*amide*, m.p. 217·5—218·5°). 2 : 3 : 5 : 6-*Tetramethylbenzyl chloride*, m.p. 67—68°, b.p. 143—144°/18 mm. *Duryl-*, m.p. 80—81°, b.p. 149—153°/6—7 mm., and 2 : 4 : 6-*triethylphenyl-acetonitrile* (**VI**), m.p. 14—16°, b.p. 127°/3—4 mm. 2 : 4 : 6-*Triethylphenyl-acetomesitylene*, b.p. 190—195°/4—5 mm. *Mesitylaceto-*2 : 4 : 6-*triethylbenzene*, b.p. 215°/9 mm. 2 : 4 : 6-*Triethylphenyl α-mesitylvinyl ketone* (**VII**), m.p. 57—57·5°. 2 : 4 : 6-$C_6H_2Me_3$·CH(OH)·CO_2H (prep. from the glyoxal by aq. KOH at 100°; 76% yield), m.p. 89—90°, with boiling red P–HI–AcOH–H_2O gives 2 : 4 : 6-*triethylphenylacetic acid* (70%), m.p. 96—96·5° (*amide*, m.p. 182·5—183°), also obtained (55%) from (**VI**). *s*-$C_6H_3Et_3$, CH_2O, and HCl at 65° give 2 : 4 : 6-*triethylbenzyl chloride*, b.p. 116—118°/4 mm. (74%) (and the ? benzylidene chloride, m.p. 82°). The enols are dehydrogenated to the vinyl ketones by $KMnO_4$ [(**IV**) also by BzO_2H]. (**IV**) and (**V**) are isomerised (HCl–MeOH) to *α-mesitylpropionyldurene*, m.p. 124·5—125°, and -iso*durene*, m.p. 85·5—86°, respectively, whence they are regenerated by NaOEt–EtOH (not by MgEtBr). In air, (**V**) gives a trace of *peroxide*, m.p. 124·5—125°. The enolic form from (**VII**) was obtained only as an oil. M.p. are corr. R. S. C.

Molecular rearrangements involving optically active radicals. X. Retention of configuration during the Wolff rearrange-

ment. J. F. Lane and E. S. Wallis (*J. Amer. Chem. Soc.*, 1941, **63**, 1674—1676; cf. A., 1941, II, 293).—Wolff rearrangement is shown to occur without inversion. It is concluded that intramol. rearrangement involving migration of a group with its electron pair occurs without Walden inversion. (+)-CPhMeBu^{a}·CO_2H (**I**), $[\alpha]^{20}_{6563}$ +18·4° in C_6H_6 (*p-bromoanilide*, m.p. 88°, $[\alpha]^{20}_{6563}$ +22·1° in C_6H_6), gives, by way of the diazoketone, $[\alpha]^{20}_{D}$ +65·0° in C_6H_6, (−)-CPhMeBu^{a}·CH_2·CO_2H, b.p. 100°/0·01 mm., α^{20}_{6563} −4·89° (l = 1) (homogeneous) (anilide, m.p. 76—77°, $[\alpha]^{20}_{6563}$ −47·0° in C_6H_6), which with CH_2N_2 gives the Me ester, b.p. 102—103°/2 mm., $[\alpha]^{20}_{6563}$ −11·2° in C_6H_6. MgPhBr then gives (−)-CPhMeBu^{a}·CH_2·CPh$_2$·OH, $[\alpha]^{20}_{D}$ −20·2° in C_6H_6, oxidised by CrO_3–AcOH to (**I**), $[\alpha]^{20}_{D}$ +20·0° in C_6H_6 (*p*-bromoanilide, m.p. 87—88°, $[\alpha]^{20}_{6563}$ +22·0° in C_6H_6). R. S. C.

Chlorophenoxyacetie acids. R. Pokorny (*J. Amer. Chem. Soc.*, 1941, **63**, 1768).—2 : 4-*Di-*, m.p. 138°, and 2 : 4 : 5-*trichlorophenoxyacetic acid*, m.p. 153°, are prepared from the phenol and CH_2Cl·CO_2H. R. S. C.

Catalytic effect of water on aminolysis of ethyl phenylacetate in *n*-butylamine.—See A., 1942, I, 106.

Chlorination of ethylenic compounds containing a reactive group by *tert.*-butyl hypochlorite in methanol.—See A., 1942, II, 72.

Condensation of benzyl carbamate with aldehydes and α-keto-acids.—See A., 1942, II, 76.

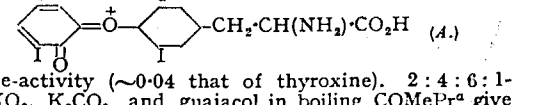
Constituents of the volatile oil of catnip. I. Nepetalic acid etc.—See A., 1942, II, 124.

Restricted rotation in arylolefines. II. Preparation and resolution of β-chloro-β-3-bromo-2 : 4 : 6-trimethyl- and -triethyl-phenylacrylic acids [and the corresponding β-methyl derivatives]. R. Adams, A. W. Anderson, and M. W. Miller (*J. Amer. Chem. Soc.* 1941, **63**, 1589—1593; cf. A., 1940, II, 85).—Whereas 2 : 4 : 6 : 3 : 1-C_6HMe_3Br·CCl:CMe·CO_2H is not racemised in boiling EtOH or Bu^{a}OH, *β-chloro-β-3-bromo-2 : 4 : 6-trimethylphenylacrylic acid* (**I**) is stable in EtOH but is slowly racemised (half-life ~200 min.) in boiling Bu^{a}OH. Models show both to be *cis*-Ar·CO_2H forms. *β-Chloro-β-3-bromo-2 : 4 : 6-triethylphenyl-α-methylacrylic acid* (**II**) could not be racemised. The above results follow expectation, but the following with glycine derivatives do not. *N-β-Chloro-β-3-bromo-2 : 4 : 6-triethylphenylacrylylglycine* (**IV**) and *N-β-chloro-β-3-bromo-2 : 4 : 6-trimethylphenyl-α-methylacrylylglycine* (**V**) could not be racemised, but *N-β-chloro-β-3-bromo-2 : 4 : 6-trimethylphenylacrylylglycine* (**VI**) has a half-life 133 min. in boiling Bu^{a}OH. These compounds are prepared by the reactions, COAr·CH_2R + MgEtBr → CHR:CAr·O·MgBr → COAr·CHR·CO_2H → (PCl_5) ClAr:CR·CO_2H → ClAr:CR·CO·NH·CH_2·CO_2H. The following are described. *3-Bromoacetomesitylene* (from 2 : 4 : 6 : 1-$C_6H_2Me_3Br$, Ac_2O, and $AlCl_3$ in CS_2), b.p. 114—115°/3 mm. *3-Bromo-2 : 4 : 6-triethyl-aceto-* (similarly prepared), b.p. 125—127°/1 mm., and *-propio-phenone*, b.p. 127—129°/1 mm. *3-Bromo-2 : 4 : 6-tri-methyl-*, m.p. 98—99° (decomp.), and *-ethyl-benzoylacetic acid*, m.p. 107—109° (decomp.), unstable. α-*3-Bromo-2 : 4 : 6-triethylbenzoylpropionic acid*, m.p. 113—115° (decomp.). dl-, m.p. 151—152°, impure *d-*, m.p. 158·5—159·5°, $[\alpha]^{20}_{D}$ +54·2° [*quinine* salt, m.p. 176·5—178° (decomp.), $[\alpha]^{20}_{D}$ −59·4°], and l-(**I**), m.p. 161—163°, $[\alpha]^{20}_{D}$ −70·8° [*quinine* salt, m.p. 184·5—186·5° (decomp.), $[\alpha]^{20}_{D}$ −105°]. dl-, m.p. 186—187°, l-, m.p. 185—186°, $[\alpha]^{28}_{D}$ −65·0° (*quinine* salt, m.p. 123—125°, $[\alpha]^{28}_{D}$ −108·5°), and d-(**VI**), m.p. 185—186°, $[\alpha]^{28}_{D}$ +59·7°. dl-(**VI**) is hydrolysed by conc. HCl to (**I**). dl-(**III**), m.p. 115—116°. dl-, l-, $[\alpha]^{28}_{D}$ −49·9° (*quinine* salt, $[\alpha]^{28}_{D}$ −115°), and d-(**IV**), (all) m.p. 185—186°, $[\alpha]^{28}_{D}$ +50·0° [*quinine* salt, m.p. 222—223° (decomp.), $[\alpha]^{28}_{D}$ −62·5°]. dl-, m.p. 146—148°, and d-(**II**), m.p. 146—148°, $[\alpha]^{28}_{D}$ +35·0° [*brucine* salt, +MeOH, m.p. 107—110° (decomp.), $[\alpha]^{28}_{D}$ −13·8°]. dl-, m.p. 179—180°, and l-(**V**), m.p. 179—180°, $[\alpha]^{26}_{D}$ −70·9° (*quinine* salt, m.p. 121·5—122·5°, $[\alpha]^{28}_{D}$ −129°). M.p. are corr. [α] are in abs. EtOH. R. S. C.

Restricted rotation in arylolefines. III. Preparation and resolution of β-chloro-β-2-methyl-1-naphthylacrylic acids. R. Adams and L. O. Binder (*J. Amer. Chem. Soc.*, 1941, **63**, 2773—2776; see preceding abstract).—2 : 1-$C_{10}H_6$MeBr (modified prep.; 84% yield), b.p. 152—156°/14 mm. (lit. 166°/13 mm.), with Mg–MgEtI–Et_2O and later solid CO_2 in C_6H_6 gives 2 : 1-$C_{10}H_6$Me·CO_2H (70%), the acid chloride (**I**) ($SOCl_2$), b.p. 145°/7 mm., of which with MgMeI–Et_2O gives 1-*aceto-2-methylnaphthalene* (89%), b.p. 125—130°/3—4 mm. With MgEtBr–Et_2O and later CO_2 (3 atm.) this gives *β-keto-β-2-methyl-1-naphthylpropionic acid* (46%), m.p. 107° (decomp.), converted by PCl_5–$POCl_3$ at, successively, < room temp., room temp., and 60° and later H_2O into *β-chloro-β-2-methyl-1-naphthylacrylic acid* (21%), m.p. 184°, which is resolved to d-, m.p. 191°, $[\alpha]^{30}_{D}$ +66° in EtOH [d-*CHPhMe·NH$_2$* salt, m.p. 158—160° (decomp.), $[\alpha]^{32}_{D}$ +42° in EtOH], and l-*forms*, m.p. 186°, $[\alpha]^{29}_{D}$ −63° in EtOH (crude *d*-CHPhMe·NH_2 salt, an oil, $[\alpha]^{32}_{D}$ −39° in EtOH), having a half-life period in boiling Bu^{a}OH ~67 min. (cf. *loc. cit.*). With MgEtBr, (**I**) gives 1-*propio-2-methylnaphthalene*, b.p. 143—144°/1—2 mm., and thence *β-keto-β-2-methyl-1-naphthylisobutyric*, m.p. 105° (decomp.), and dl-, m.p. 161—162°, d- and l-*β-chloro-β-2-methyl-1-naphthyl-α-methylacrylic acid*, m.p. 123°, $[\alpha]^{26}_{D}$ +55°, −58° in EtOH [*quinine* salts, m.p. 194° (decomp.) and 132° (decomp.), $[\alpha]^{26}_{D}$ −72° and −136° in EtOH, respectively], having in boiling Bu^{a}OH a half-life period ~70 hr. M.p. are corr. R. S. C.

Synthesis of *dl*-3 : 5-di-iodo-4-(2′ : 4′-di-iodo-3′-hydroxyphenoxy)phenylalanine, a physiologically inactive isomeride of thyroxine. C. Niemann and C. E. Redemann (*J. Amer. Chem. Soc.*, 1941, **63**, 1549—1552).—4 : 2 : 6 : 1-NO_2·$C_6H_2I_2$·NH_2 (improved prep.), m.p. 249—250°, yields (diazo-method) 88% of pure 3 : 4 : 5 : 1-$C_6H_2I_2$·NO_2, m.p. 164—166°, which with *m*-OMe·C_6H_4·OH and anhyd. K_2CO_3 in boiling COMePr^{a} gives 3 : 5-*di-iodo*-4-m-*anisoxynitrobenzene* (76%), m.p. 140—141°, reduced by $SnCl_2$–HCl–AcOH to 3 : 5-*di-iodo*-4-m-*anisoxyaniline* (90%), m.p. 135—136° (impure hydrochloride, m.p. variable, 86° to 123°; *picrate*, m.p. 156—157°; *Ac* derivative, m.p. 176—177°). This is converted by HCl–AcOH, followed by Bu^{a}O·NO at <20° and then aq. KCN–$CuSO_4$ at, successively, <10°, room temp., and 80°, into 3 : 5-*di-iodo*-4-m-*anisoxybenzonitrile* (60%), m.p. 156—157°, hydrolysed by HI–AcOH to the corresponding *acid*, m.p. 203° (decomp.), and reduced by $SnCl_2$–HCl–Et_2O to the *aldehyde* (75%), m.p. 145—146° (2 : 4-*dinitrophenylhydrazone*, m.p. 276—277°). Hippuric acid etc. then yields 2-*phenyl*-4-3′ : 5′-*di-iodo*-4′-m-*anisoxybenzylideneoxazol*-5-*one*, sinters at 163°, m.p. 166—168°, hydrolysed by NaOH–H_2O–EtOH to *α-benzamido-β*-3 : 5-*di-iodo*-4-m-*anisoxyphenylacrylic acid*, m.p. 212—213°, which is converted by boiling HI–AcOH–red P into *α-amino-β*-3 : 5-*di-iodo*-4-m-*hydroxyphenoxyphenylpropionic acid* (39%), m.p. 229—231°. With I–KI–NH_4–H_2O at <5° this gives dl-*α-amino-β*-3 : 5-*di-iodo*-4-2′ : 4′-*di-iodo*-3′-*hydroxyphenoxyphenylpropionic acid* (87%), m.p. 202°, which is inactive at levels up to 500 mg. per kg. body-wt. (rats). The analogous method is also superior to that of Harington *et al.* (A., 1927, 358) for synthesis of *dl*-thyroxine. R. S. C.

Synthesis of *dl*-3 : 5 : 3′ : 5′-tetraiodo-4-2′-hydroxyphenoxyphenylalanine, a physiologically active isomeride of thyroxine. C. Niemann and J. F. Mead (*J. Amer. Chem. Soc.*, 1941, **63**, 2685—2687).—dl-3 : 5 : 3′ : 5′-*Tetraiodo*-4-2′-*hydroxyphenoxyphenylalanine* (**I**), which can, by loss of H^+ and $2e^-$, assume the quinonoid form (*A*) (see preceding abstract), has



(*A.*)

thyroxine-activity (~0·04 that of thyroxine). 2 : 4 : 6 : 1-$C_6H_2I_2$·NO_2, K_2CO_3, and guaiacol in boiling COMePr^{a} give 3 : 5-*di-iodo*-4-o-*anisoxynitrobenzene*, m.p. 148—150°, reduced by $SnCl_2$,H_2O in hot AcOH to 3 : 5-*di-iodo*-4-o-*anisoxyaniline hydrochloride*, m.p. 237° after sintering (*Ac* derivative, m.p. 225—227°, of the free base), which with Bu^{a}O·NO in AcOH–H_2O, followed by aq. KCN–$CuSO_4$, gives 3 : 5-*di-iodo*-4-o-*anisoxybenzonitrile*, m.p. 135—137°. This is hydrolysed to the *acid*, m.p. 253—254° after sintering, and reduced (Stephen) to the *aldehyde*, m.p. 249—250°. Thence is obtained 2-*phenyl*-4-3′ : 5′-*di-iodo*-2′-*methoxyphenoxybenzylidene*-5-*oxazolone*, m.p. 198—200°, converted by red P–HI–AcOH into dl-3 : 5-*di-iodo*-4-2′-*hydroxyphenoxyphenylalanine*, m.p. 240° (decomp.), which with aq. I–KI–NaOH–NH_3 gives (**I**), m.p. 218—219° (decomp.). R. S. C.

Mutarotation of a β-lactone. E. P. Kohler and C. L. Bickel (*J. Amer. Chem. Soc.*, 1941, **63**, 1531—1532; cf. A., 1934, 523, 1217).—*d*-CH_2Bz·CHPh·CO_2H (Bickel, A., 1938, II, 236) gives the *α-Br-acids*, (**I**) an oil, [α] +157°, and (**II**) m.p. 148°, [α] +90°. (**I**) readily gives *γ-keto-αγ-diphenyl-β-butyrolactone* (**III**), m.p. 75°, [α] +155° (extrapolated), but

(II) gives the isomeric *lactone* (IV), m.p. 130°, [α] +92°. In MeOH, (III) suffers rapid loss of α (structure of the intermediate discussed), followed by a much slower gain in α due to formation of d-*γ-keto-β-methoxy-αγ-diphenyl*-n-*butyric acid*, m.p. 132°, [α] +153°. *l*-$CH_2Bz{\cdot}CHPh{\cdot}CO_2H$ gives the *l*-isomerides of (II)—(V), which, when mixed with the *d*-, give the known *dl*-compounds. In MeOH, the *dl*-lactone gives dl-*γ-keto-β-methoxy-αγ-diphenyl*-n-*butyric acid*, m.p. 117°. (IV) shows no mutarotation in MeOH. [α] are $[\alpha]_D^{25}$ in MeOH. R. S. C.

Ethyl γ-2-carbethoxy-2-*cyclo*hexanonyl-*n*-butyrate and related compounds. C. S. Marvel and L. A. Brooks (*J. Amer. Chem. Soc.*, 1941, **63**, 2853).—*Et γ-2-carbethoxy*-2-cyclo*hexanonyl*-n-*butyrate* (prep. from Et *cyclo*hexanone-2-carboxylate and $Br{\cdot}[CH_2]_3{\cdot}CO_2Et$), b.p. 166—168°/2 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 84—85°), is hydrolysed by dil. NaOH to *γ-2-cyclo*hexanonyl-*n*-butyric acid and hydrogenated (Raney Ni; 125°/2500 lb.; EtOH) to *Et 2-hydroxy*-1-*carbethoxy*cyclo*hexyl*-n-*butyrate*, b.p. 164—166°/2 mm. 1-Δ^{δ}-*Pentenylidene*-, b.p. 119—121°/3 mm., and 3-*phenyl*-1-Δ^{δ}-*pentenylidene-hydrindene*, m.p. 190—191°, are prepared by condensation of 1-hydrindone and 3-phenylhydrindone, respectively, with $CH_2{:}CH{\cdot}[CH_2]_3{\cdot}MgBr$ and dehydrating the resulting alcohol by distillation. cyclo*Pentylidene*cyclo*pentanone*-2 : 4-*dinitrophenylhydrazone* has m.p. 228—229°. R. S. C.

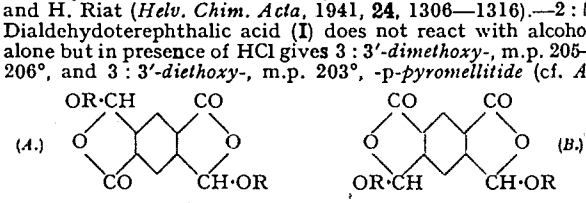
Rosenmund–von Braun nitrile synthesis. C. F. Koelsch and A. G. Whitney (*J. Org. Chem.*, 1941, **6**, 795—803).—The reaction ArX + CuCN → ArCN + CuX at 250° has a marked induction period but on the basis of the total time required for 50% conversion the compounds studied can be arranged in the sequence of increasing reactivities: *p*-$C_6H_4Br{\cdot}CHPh_2$ (I) < *m*-C_6H_4MeBr < *p*-$C_6H_4Br{\cdot}COPh$ < *o*-C_6H_4MeBr < PhBr < 2 : 4 : 6 : 1-$C_6H_2Me_3Br$ < 1-$C_{10}H_7Br$ < *p*-$C_6H_4Br{\cdot}CO_2H$. In most cases the customary 6-hr. period of heating can be replaced by 2 hr. Addition of small amounts of *p*-$C_6H_4Me{\cdot}CN$ (II) to (I) and CuCN greatly increases the extent to which the reaction proceeds in a given time but with larger amounts of (II) the change slows down, showing that the diluting effect of (II) outweighs its catalytic influence. (II) does not completely abolish the induction period, showing that the initial inhomogeneity of the reaction mixture is not the only factor responsible for the induction period. The presence of quinol almost doubles the induction period of PhBr and CuCN. $CuSO_4$ exerts a marked promoting effect on the reaction of (I) and CuCN; part of the usual induction period is therefore due to the necessity for some oxidation of Cu^{I} to Cu^{II}. The sp. catalytic power of Cu salts may be explained by the mechanism: $ArX + Cu^{++} \rightleftharpoons [ArX \rightarrow Cu]^{++} \rightarrow (+ Cu^{+})\ Cu^{++} \rightarrow [ArX \rightarrow Cu]^{+}$ (III); (III) → CuX + Ar^{+}. It is assumed that only Cu^{++} can form a stable complex with a halide through interaction with the halogen. In the absence of reducing agent (Cu^{+}) this complex can only revert to the substances from which it was formed but a Cu^{I} salt converts it into a new complex which can decompose to an aryl ion, which can combine with any anion present. The synthesis is conveniently effected by placing the mixture of ArHal and CuCN with a few drops of (II) and little $CuSO_4$ in a bath heated by boiling Ph_2. Completion of the reaction is indicated by a marked diminution in the vol. of solid Cu salts and formation of a dark, liquid phase and usually follows in 10—30 min. H. W.

Identification of nitriles.—See A., 1942, II, 124.

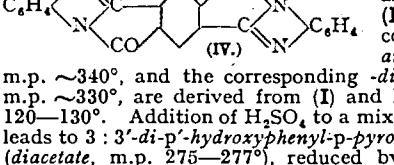
Fries rearrangement of esters of hindered acids. R. C. Fuson, S. L. Scott, and S. B. Speck (*J. Amer. Chem. Soc.*, 1941, **63**, 2845—2846).—p-*Tolyl* 2 : 6-*dimethyl*-, m.p. 62·5—63°, and 4-*methoxy*-2 : 6-*dimethyl-benzoate*, m.p. 73°, with $AlCl_3$ at 150° readily give 4-*hydroxy*-3-2′ : 6′-*dimethyl*-, m.p. 89·7—90·7° (corr.), and -3-4′-*methoxy*-2′ : 6′-*dimethyl-benzoyltoluene*, m.p. 86°. Absence of steric hindrance indicates that rearrangement does not proceed by fission to the phenol and acid chloride (cf. Skraup *et al.*, A., 1925, i, 143). R. S. C.

Mesitoic [2 : 4 : 6-trimethylbenzoic] anhydride. R. C. Fuson, J. Corse, and N. Rabjohn (*J. Amer. Chem. Soc.*, 1941, **63**, 2852—2853).—2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CO_2Na$ and 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}COCl$ in C_5H_5N at 150° give 2 : 4 : 6-*trimethylbenzoic anhydride*, m.p. 106—107°, identified by hydrolysis to the acid and by conversion by 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}MgBr$ into dimesityl ketone. R. S. C.

2 : 5-Dialdehydobenzene-1 : 4-dicarboxylic acid and 4 : 6-dialdehydobenzene-1 : 3-dicarboxylic acid. H. de Diesbach and H. Riat (*Helv. Chim. Acta*, 1941, **24**, 1306—1316).—2 : 5-Dialdehydoterephthalic acid (I) does not react with alcohols alone but in presence of HCl gives 3 : 3′-*dimethoxy*-, m.p. 205—206°, and 3 : 3′-*diethoxy*-, m.p. 203°, -p-*pyromellitide* (cf. *A*).



Similarly 4 : 6-dialdehydo*iso*phthalic acid (II) affords 3 : 3′-*dimethoxy*-, m.p. 192—193°, and 3 : 3′-*diethoxy*-, m.p. 202°, -m-*pyromellitide* (cf. *B*). (I) and PCl_5 at 100° affords 3 : 3′-*dichloro*-p-*pyromellitide*, m.p. 256°, in which Cl is very firmly retained. Ac_2O containing a little conc. H_2SO_4 at 100° transforms (I) into 3 : 3′-*diacetoxy*-p-*pyromellitide*, m.p. 276—278°. In presence of aq. alkali (I) and COPhMe give unidentified products, whereas in presence of NaOEt 3 : 3′-*diphenacyl*-p-*pyromellitide*, m.p. 306—307° (decomp.), results. The product is insol. in alkali carbonates and very slowly sol. in NaOH; when freshly prepared it appears to be in the normal form since it is sol. in alkali carbonates and gives a Na salt sol. in H_2O. With *o*-$C_6H_4Ac{\cdot}CO_2H$ (I) affords 3 : 3′-*di-o*′-*carboxyphenacyl*-p-*pyromellitide*, decomp. without melting >325°, and with $CH_2Ph{\cdot}CN$ and NaOEt–EtOH it gives 2 : 5-*di-α-cyanostyrylterephthalic acid*, m.p. 291°. Analogously $CN{\cdot}CH_2{\cdot}CO_2Et$ yields 2 : 5-*di-β-cyano-β-carbethoxyvinylterephthalic acid*, m.p. 212·5°. (I) gives a *dioxime* which becomes converted into the corresponding di-imine at ~150° whereas only decomp. products are obtained from (II) under like conditions. With $N_2H_4{\cdot}H_2O$ in boiling EtOH (I) gives p-*pyromellitdiazone*, m.p. >350°, with $NHPh{\cdot}NH_2$ in hot AcOH (I) and (II) afford respectively *diphenyl*-p-, m.p. 362°, and -m-, m.p. 340°, *-pyromellitdiazone*. $(NHPh)_2$ and (I) give 3 : 3′-*di-αβ-diphenylhydrazino*-p-*pyromellitide*, m.p. ~238° (decomp.). (I) and NH_2Ph yield 2 : 5-*dianilomethylterephthalic acid*, m.p. 281° (decomp.); similar *compounds*, m.p. 282° (decomp.), 325°, decomp. ~350°, and decomp. ~340° are obtained from (I) and *p*-$C_6H_4Me{\cdot}NH_2$, *p*-$NH_2{\cdot}C_6H_4{\cdot}N_2Ph$, *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$, and p-$NH_2C_6H_4{\cdot}OH$. (II) similarly yields *substances*, m.p. 262° and m.p. 263°, with NH_2Ph and *p*-$C_6H_4Me{\cdot}NH_2$. (I) and *o*-$C_6H_4(NH_2)_2$ (III) in boiling EtOH gave a mixture of substances, whereas the anhydride of (I) and (III) at 120—130° afford the dilactam (IV), m.p. ~300° (decomp.). 3 : 2′-*Dibenzamido*-p-*pyromellitide*, m.p. ~340°, and the corresponding *-diacetamido*-compound, m.p. ~330°, are derived from (I) and NH_2Bz or NH_2Ac at 120—130°. Addition of H_2SO_4 to a mixture of (I) and PhOH leads to 3 : 3′-*di*-p′-*hydroxyphenyl*-p-*pyromellitide*, m.p. >310° (*diacetate*, m.p. 275—277°), reduced by Zn and NaOH to 2 : 5-*di*-p-*hydroxybenzylterephthalic acid*, m.p. 327° (decomp.). (II) does not react in this manner. H. W.



Structural models of cortin compounds in the naphthalene series. L. Long, jun., and A. Burger (*J. Org. Chem.*, 1941, **6**, 852—857).—A decahydronaphthalene derivative with a ketol side-chain at $C_{(1)}$ has been synthesised as a simple model of the cortin series. 1-Keto- is hydrogenated (PtO_2 in 95% EtOH at room temp. and atm. pressure) to 1-*hydroxy*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (I), b.p. 109°/1 mm. (α-*naphthylurethane*, m.p. 131—133°). Attempts to replace OH by Br in (I) by means of 48% HBr at room temp. lead to loss of HBr and production of 6-*methoxy*-3 : 4-*dihydronaphthalene*, m.p. 73—74°. Treatment of (I) in dry C_6H_6 containing anhyd. $CaCl_2$ with HCl at 0° and of the oily residue with KCN–KI–$CuSO_4$ at 0° followed by alkaline hydrolysis yields an alkali-sol. resin and a colourless *liquid*, (?) $C_{14}H_{16}O$, b.p. 107—108°/2 mm., which forms a red picrate of low m.p. 1 : 6-$C_{10}H_6I{\cdot}OMe$ and dry CuCN at 220—230° give 6 : 1-$OMe{\cdot}C_{10}H_6{\cdot}CN$, m.p. 78—79°, slowly transformed by KOH in boiling $Pr^{\alpha}OH$ into 6 : 1-$OMe{\cdot}C_{10}H_6{\cdot}CO_2H$ (II), m.p. 182—182·5°, and by KOH in EtOH or $Pr^{\beta}OH$ into approx. equal amounts of (II) and 6-*methoxy*-1-*naphthoamide*, m.p. 201—203°. (II) is converted by boiling 48% HBr–glacial AcOH into 6 : 1-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$, m.p. 212·5—213° [*Et* ester (III), m.p. 105—107°], which is hydrogenated (PtO_2 in glacial AcOH; room temp.; 760 mm.) to *decahydro*-1-

naphthoic acid (IV) (probably a mixture of stereoisomerides), m.p. 96—123° and, after re-solidification, m.p. 112—115°. Variations in the experimental conditions including the use of (III) or 6 : 1-OAc·$C_{10}H_6$·CO_2H do not give a product containing an alcoholic OH or its acetate. (IV) is converted by successive treatments with $SOCl_2$ in C_6H_6–C_5H_5N, CH_2N_2 in C_6H_6, and 2N-HSO_4 in dioxan at 40° into 1-*α-keto-β-hydroxyethyldecahydronaphthalene*, m.p. 82·5—83°. H. W.

Effect of esterification of the reactants on the mechanism of the transamination reaction.—See A., 1942, II, 77.

Condensation of aldehydes with malonic acid. XHI. Condensation of *o*-, *m*-, and *p*-chlorobenzaldehyde and of *m*-bromobenzaldehyde. Influence of groups and comparison with Perkin's reaction. K. C. Pandya and (Miss) R. B. Pandya (*Proc. Indian Acad. Sci.*, 1941, **14**, A, 112—122).—Condensation of PhCHO and the four halogenated derivatives with $CH_2(CO_2H)_2$ in presence of a trace of C_5H_5N but no other condensing agent gives invariably excellent and sometimes quant. yields of products. The presence of Cl_2 or Br accelerates the reactions and improves the yields. The yields are ≫ those obtained by Perkin's method, the condensations are quicker, and the products cleaner. The following appear new: p-*chlorobenzylidenemalonic acid*, m.p. 197—198° (decomp.) (*Et*$_2$ ester, m.p. 237°); m-*chloro-*, m.p. 184—186°, and m-*bromo-*, m.p. 192° (decomp.), *-benzylidenemalonic acid*. H. W.

Friedel–Crafts reaction. V. Effect of polar substituents on the reactivity of *para*-substituted phenylsuccinic anhydrides with simple aromatic hydrocarbons. M. A. Wali, A. K. Khalil, R. L. Bhatia, and S. S. Ahmad (*Proc. Indian Acad. Sci.*, 1941, **14**, A, 139—150).—The influence of *p*-substitution in phenylsuccinic anhydride (I) on the condensation of the anhydride with simple aromatic hydrocarbons in presence and absence of $PhNO_2$ has been examined. (I) with C_6H_6 in $PhNO_2$ containing $AlCl_3$ or in C_6H_6 alone gives a mixture of CHPhBz·CH_2·CO_2H, m.p. 168°, and CH_2Bz·CHPh·CO_2H, m.p. 154°. A similar mixture is obtained when PhMe replaces C_6H_6. Analogous condensations lead to: *β-benzoyl-β-*, m.p. 185°, and *-α-p-nitrophenylpropionic acid*, m.p. 167°, which gives the characteristic pyrylium and piperonylidene salt reactions: *β-p-toluoyl-β-*, m.p. 178°, and *-α-p-nitrophenylpropionic acid*, m.p. 173°; *β-benzoyl-α-p-anisylpropionic acid*, m.p. 158°; *β-toluoyl-β-*, m.p. 147°, and *-α-p*-anisylpropionic acid, m.p. 158°; *β-benzoyl-β-*, m.p. 166°, and *-α-p-chlorophenylpropionic acid*. Clemmensen reduction of the requisite CO-acids affords *β-phenyl-γ-p-tolyl-*, m.p. 104°, *γ-phenyl-β-p-chlorophenyl-*, m.p. 86°, and *γ-phenyl-α-p-chlorophenyl-*, m.p. 150°, *-butyric acid*. p-*Chlorophenylsuccinic acid*, m.p. 205° (*anhydride*, m.p. 80°), appears to be new. H. W.

Behaviour of 3-methylphthalic anhydride in Friedel–Crafts and Grignard condensations. M. S. Newman and C. D. McCleary (*J. Amer. Chem. Soc.*, 1941, **63**, 1542—1544).—3-Methyl-1 : 2 : 3 : 6-tetrahydrophthalic anhydride (I) [prepared from CH_2:CH·CH:CHMe and (CH·CO)$_2$O (best, 40% excess; 80·6% yield) in C_6H_6 at 5—10° (20 days)], m.p. 59—62°, b.p. 131—134°/5 mm., and Br in boiling AcOH give a Br-compound, converted at 210—220° into 3 : 1 : 2-C_6H_3Me(CO)$_2$O (II) (73%), m.p. 114·5—117°. Dehydrogenation of (I) by S gives with difficulty 50% of (II), $Pb(OAc)_4$ gives only very little, and Pd–C at 270—320° or Ni–kieselguhr at 350—370° give none although 50% of the expected H_2 is evolved. With MgPhBr in Et_2O–C_6H_6, (II) gives 2 : 6 : 1-(III) (44%), m.p. 123—125°, and 3 : 2 : 1-C_6H_3MeBz·CO_2H (IV) (14%), m.p. 172·0—172·9°, and *αα-diphenyl-3-methylphthalide* (V) (3·7%), m.p. 114·8—116°. With $AlCl_3$ in C_6H_6, (II) gives (III) 23·4, (IV) 38·5, and (V) 9·5%. MgPhBr in Et_2O–C_6H_6 converts (III) into (V), thus proving the structure of (V). Separation of (III) and (IV) is effected quantitatively by HCl–MeOH and subsequent treatment with H_2SO_4, the normal and *ψ*-esters of (III) being hydrolysed and the (normal) ester of (IV) remaining unchanged. M.p. are corr. R. S. C.

Naphthaldehydes. HI. Derivatives of 5-bromo-1-naphthaldehyde and of 1-naphthaldehyde. P. Ruggli and R. Preuss (*Helv. Chim. Acta*, 1941, **24**, 1345—1359; cf. A., 1940, II, 222).—1-$C_{10}H_7$·CH_2Cl (prep. described from $C_{10}H_8$, 30% CH_2O, conc. HCl, and conc. H_2SO_4 and from $C_{10}H_8$, solid paraformaldehyde, and conc. HCl in AcOH) is converted by $(CH_2)_6N_4$ in boiling 60% EtOH into 1-$C_{10}H_7$·CHO (I), b.p. 156—157°/14 mm., transformed by Br in $CHCl_3$ into 5 : 1-$C_{10}H_6$Br·CHO (II), m.p. 104—105°, with a small proportion of 5 : 1-$C_{10}H_6$Br·CO_2H. (II) yields an *anil*, m.p. 103—104°, *phenylhydrazone*, m.p. 104—105°, p-*nitro-*, m.p. 267—268°, and 2 : 4-*dinitro-*, m.p. 221—222° (decomp.), *-phenylhydrazone*; with NPhMe$_2$ and $ZnCl_2$ at 100° it yields *bromonaphthyltetramethyldiaminodiphenylmethane*, m.p. 158—160°, oxidised by PbO_2 in HCl to a black-green dye. With $CH_2(CO_2H)_2$ and C_6H_5N at 40—45° and then at 100° (II) yields 5-*bromonaphthylacrylic acid* (III), m.p. 269—270°. Gradual addition of (II) to HNO_3 (*d* 1·47) at −5° and subsequently at room temp. yields 5-*bromo*-8-*nitro*-1-*naphthaldehyde* (IV) (*Et*$_2$ *acetal*, m.p. 94—95°; p-*nitro-*, m.p. 205—207°, and 2 : 4-*dinitro-*, decomp. 243—244°, *-phenylhydrazone*); with NH_2Ph in warm alcohol it gives a Br-free compound. (III) is nitrated by conc. HNO_3 (*d* 1·47) at −5° and then at room temp. to 5-*bromo*-8-*nitro*-1-*naphthylacrylic acid* (V), m.p. 141—142° (*Me* ester, m.p. 128—129°), also obtained from (IV), $CH_2(CO_2H)_2$, and C_5H_5N at 40—45° and then at 100°. Reduction of (V) by $SnCl_2$ or $(NH_4)_2S$ gives ill-defined dark green or black amorphous compounds. (V) is transformed into its *dibromide*, m.p. 197—198° (*Me* ester, m.p. 196—197°), by irradiation in an excess of Br. (I), $CH_2Ph·CO_2Na$, Ac_2O, and $ZnCl_2$ at 100° yield *α-phenyl-β-1-naphthylacrylic acid*, m.p. 160—161°; it is decarboxylated by Cu powder in quinoline at 220—230° to a brown oil which gives a yellow *picrate*, m.p. 198—199°. With 1 ; 2 : 4-C_6H_3Me$(NO_2)_2$ and piperidine at 130—140°, (I) gives *β-2 : 4-dinitrophenyl-α-1-naphthylethylene*, m.p. 227—228°, which with Br in $CHCl_3$ yields an *α-dibromide*, m.p. 161—162°, transformed into the parent material by C_5H_5N, and a *β-dibromide*, m.p. 98—100° (decomp.), converted by C_5H_5N into *α-bromo-β-2 : 4-dinitrophenyl-α-1-naphthylethylene* (VI), m.p. 206—208°. Exposure to sunlight of (VI) in C_5H_5N gives 6-*nitro*-2-1-*naphthylisatogen*, m.p. 223—225°. The *anilide*, m.p. 216—217°, and p-*bromophenacyl* ester, m.p. 131—132°, of 5 : 1-$C_{10}H_6$Br·CO_2H are described. H. W.

Nuclear methylation of β-resorcylaldehyde. T. R. Seshadri and V. Venkateswarlu (*Proc. Indian Acad. Sci.*, 1941, **14**, A, 297—306).—A survey of past work on the nuclear methylation and ethylation of derivatives of *m*-$C_6H_4(OH)_2$ and 1 : 3 : 5-$C_6H_3(OH)_3$ is given and a mechanism for the reaction is suggested. Treatment of *β*-resorcylaldehyde with KOH and MeI in anhyd. MeOH, first in a freezing mixture, then at room temp., and finally at the b.p. of the mixture, gives exclusively 2-*hydroxy*-4-*methoxy*-m-*tolualdehyde* (I), m.p. 64—65°, which does not undergo a Perkin reaction with Ac_2O and NaOAc. 2 : 1 : 3-C_6H_3Me$(OH)_2$ (II) is converted by Zn(CN)$_2$ and HCl in anhyd. Et_2O followed by hydrolysis of the aldimine hydrochloride into 2 : 4 : 3 : 1-$(OH)_2C_6H_2$Me·CHO, m.p. 150° after slight softening at 137°, methylated (MeI and K_2CO_3 in boiling $COMe_2$) to (I). Condensation of (I) with $CH_2(CO_2Et)_2$ in presence of piperidine affords *Et* 7-*methoxy*-8-*methylcoumarin*-3-*carboxylate*, m.p. 159—160°; the corresponding *acid*, m.p. 211—212°, is decarboxylated (Cu-bronze in quinoline at 150—160°) to 7-*methoxy*-8-*methylcoumarin* (III), m.p. 122—123°. (II), malic acid, and conc. H_2SO_4 at 120° give 7-*hydroxy*-8-*methylcoumarin*, m.p. 231—232°, also obtained by reduction (H_2–Pd–C in glacial AcOH) of 7-hydroxycoumarin-8-aldehyde and methylated (K_2CO_3–MeI in boiling $COMe_2$) to (III). H. W.

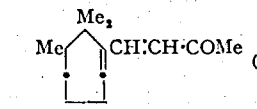
Keto-carbinylamines, COR·CH_2·CR′R″·NH_2. C. E. Rehberg [with H. R. Henze] (*J. Amer. Chem. Soc.*, 1941, **63**, 2785—2789).—Condensation of CH_2:CH·CH_2·MgBr (I) with alkoxy-nitriles (Allen *et al.*, A., 1939, II, 409; since shown to be a general reaction of nitriles) is extended to CH_2Bz·CN. MgEtBr or MgPr^{n}Br adds to the "enol" [imine] form of CH_2Bz·CN in Et_2O and the product is converted by NH_4Cl–ice into the imine and a dimeride: a *dimeride*, $C_{18}H_{14}O_2N_2$, m.p. 166°, and *γ-imino-α-phenyl-n-hexan-α-one*, m.p. 93—94°, are described. Only tars are thus obtained from (I). CH_2Bz·CMe:NH (II), m.p. 142—144° (corr.), is obtained by condensing COPhMe and EtOAc by Na (cf. Beyer *et al.*, A., 1887, 943) to give COPh·CH_2·COMe, m.p. 60—61°, and heating this with NH_3–abs. EtOH at 110°. The product from (I) and (II) is decomposed by NH_4Cl–ice to give *γ*-amino-*α*-phenyl-*γ*-methyl-Δ^{ε}-hexen-*α*-one (III), an oil, which loses NH_3 at room temp. or rapidly at 50—60°, but not in acid. Distillation of (III) gives *α-phenyl-γ-methyl-*$\Delta^{\beta\varepsilon}$*-hexadien-α-one* (IV), b.p. 135—137°/10 mm. Hydrogenation (PtO_2, 95% EtOH) of (III) gives *γ-amino-α-phenyl-γ-methyl-n-hexan-α-one*

[*picrate*, m.p. (+0·5H_2O) 93—94° or (anhyd.) 153—154°, resolidifies at 156—160°, remelts at 180—185° (decomp.)], converted by distillation into NH_3 and *α-phenyl-γ-methyl-*Δ^{β}*-n-hexen-α-one* (**V**), b.p. 123—125°/5 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 140—141° (corr.)]. Hydrogenation (PtO_2) of (**IV**) or (**V**) in EtOH gives *β-methyl-n-hexophenone*, b.p. 105—108°/3 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 139—140° (140—141°) (corr.)]. The structure of the compounds is proved by *n* of (**V**) and synthesis of (**V**) and (**VI**) from MgPhBr + $CMePr^{\alpha}$:CH·CN and $CHMePr^{\alpha}CH_2$·MgBr + PhCN, respectively. Similarly are prepared γ-amino-α-phenyl-γ-ethyl-Δ^{ϵ}-*n*-hexen-α-one [*picrate*, m.p. 110—111° (corr.)] and -*n*-hexan-α-one [*picrate*, m.p. 129—130°, resolidifies at 135—140°, remelts at 180—185° (decomp.; corr.)], *α-phenyl-γ-ethyl-*$\Delta^{\beta\epsilon}$*-hexadien-α-one*, b.p. 130—132°/2 mm. [2 : 4-dinitrophenylhydrazone, m.p. 131—133° (corr.)], and -*n-hexan-α-one*, b.p. 130—132°/5 mm. [2 : 4-dinitrophenylhydrazone, m.p. 130—131° (corr.)]. Ozonolysis of (**V**) in light petroleum gives BzOH and HCO_2H with traces of COPhMe and COMePr. Loss of NH_3 from the amines resembles loss of OH from *tert.*-alcohols. R. S. C.

Mechanism of aromatic side-chain reactions, with special reference to the polar effects of substituents. X. Physical and chemical evidence relating to the polar effect of *o*-methyl substituents in derivatives of type $C_6H_2Me_3$·CO·CH_2R. J. W. Baker and W. T. Tweed (*J.C.S.*, 1941, 796—802; cf. A., 1938, II, 234; 1940, I, 295).—2 : 4 : 6 : 1-$C_6H_2Cl_2$·COCl and MgMeI–Et_2O afford 2 : 4 : 6 : 1-$C_6H_2Cl_3$·COMe (**I**), m.p. 50°, and a *compound*, m.p. 192° (? 2 : 4 : 6-trichlorophenacyl-2 : 4 : 6-trichlorophenylmethylcarbinol or β-2 : 4 : 6-trichlorophenyl*iso*propyl 2 : 4 : 6-trichlorobenzoate). , (**I**) and Br, without solvent, give 2 : 4 : 6-*trichlorophenacyl bromide*, m.p. 81°. 2 : 4 : 5-*Trichlorobenzonitrile*, m.p. 104° (prepared from 2 : 4 : 5 : 1-$C_6H_2Cl_2$·N_2X), is hydrolysed to the amide by H_2SO_4 at room temp., then at 100° (bath), and then refluxing for 1 hr., and the cold mixture is then treated with $NaNO_2$, giving 2 : 4 : 5 : 1-$C_6H_2Cl_3$·CO_2H (**II**) and thence the *chloride* (**III**), m.p. ~28°, b.p. 125°/2 mm. (**III**) and MeI–Zn give different products under different conditions, *e.g.*, *compounds*, m.p. 228° ($C_{16}H_{10}O_2Cl_6$) and m.p. 64°, have been isolated; (**III**)–MeI–Zn in C_6H_6 at 0°, then at 100° (bath), afford 2 : 4 : 5-*trichloroacetophenone* (**IV**), m.p. 47°, b.p. 128—132°/1·5 mm., together with (**II**) and a compound, m.p. 130°. (**IV**) and Br in light petroleum give 2 : 4 : 5-*trichlorophenacyl bromide*, m.p. 60° [C_5H_5N yields the *pyridinium bromide*, m.p. 227° (decomp.)]. The heat of combustion of 2 : 4 : 6 : 1-$C_6H_2Me_3$·COMe (**V**) is < that of the 2 : 4 : 5 : 1-isomeride (**VI**), indicating a slightly larger resonance energy in the mol. of (**V**). Further support for the contention that resonance occurs between the electrons of the C–H bonds of the Me and those of the CO groups is indicated by a comparison of the mol. refractivities [that of (**V**) exhibits a greater exaltation than does that of (**VI**), suggesting increased conjugation] and of the basic character of the O of the CO of (**V**) and (**VI**) and of (**I**) and (**IV**). Whereas the basic strength of (**VI**) is similar to that of COPhMe, (**V**) is as weak a base as is (**I**). (**V**) has a slightly lower heat of combustion than has (**VI**). The large difference in magnitude between the reaction velocities (with C_5H_5N in dry $COMe_2$) of 2 : 4 : 5-*trimethylphenacyl bromide*, m.p. 57° [from (**VI**) and Br without solvent], and the 2 : 4 : 6-isomeride is similar to that observed with the corresponding trichlorophenacyl bromides; the large inhibitory effect of the two *o*-substituents is due mainly to spatial factors. A. T. P.

Substances with the odour of violets. XI. Physical constants and crystalline derivatives of irone before and after boiling with dilute sulphuric acid. L. Ruzicka, C. F. Seidel, and G. Firmenich (*Helv. Chim. Acta*, 1941, **24**, 1434—1449).—All samples of irone previously investigated, both natural products and those obtained by treatment with dil. H_2SO_4, correspond with a ketone of the structure of α-irone. β-Irone may possibly be present in small amount in the natural product and may be produced in somewhat larger proportion by displacement of the double linking into the conjugated position by treatment with acids. Certain evidence for this possibility, in the shape of a cryst. derivative, is not at present available. The absorption spectrum and physical consts. of natural irone are much more similar to those of α- than those of β-ionone. Hence (**I**) and (**II**) are designated α- and β-irone respectively. Irone, regenerated from cryst. derivatives, has (mean vals.) b.p. 136—138°/10 mm., $[\alpha]_D$ +70° in EtOH (*p*-bromophenylhydrazone, m.p. ~170°; phenylsemicarbazone, m.p. ~170°; thiosemicarbazone, m.p. ~120°).

(I.)



(II.)

Tetrahydroirone, b.p. 135—136°/10 mm., α_D −135°, gives a semicarbazone (**III**), m.p. 203—204°, *p*-nitrophenylhydrazone, m.p. 138—139°, and 2 : 4-dinitrophenylhydrazone, m.p. 113—114°. The mother-liquors from (**III**) give *semicarbazones*, m.p. 173—175° and 160—161° respectively, from which are isolated *tetrahydroirones*, b.p. 137—138°/10 mm., α_D +5°, and b.p. 134—135°/10 mm., α_D +6·5°. Treatment of irone with boiling 20% H_2SO_4 for 10 hr. causes little resinification. The product is converted into the phenylsemicarbazone which is separated into four fractions. The properties of the irone regenerated from each fraction are very closely similar and the tetrahydroirones obtained therefrom agree in properties among themselves and with those of the product from untreated irone. An essential difference is observed only in the thiosemicarbazones; those derived from the different fractions all have m.p. 175—180°. Further treatment with boiling 20% H_2SO_4 for 10 hr. leaves the physical consts. unchanged but the product gives small amounts of a tetrahydroirone, α_D +1·2° (*semicarbazone*, m.p. 162—164°; 2 : 4-*dinitrophenylhydrazone*, m.p. 111—113°). The thiosemicarbazones, m.p. 179—180° and m.p. 120—122°, of the acid-treated and natural irones give closely similar absorption spectra so that the difference between them is not due to a different arrangement of the double linkings. Irone is converted by $(CH{\cdot}CO)_2O$ at 150° into an amorphous adduct, converted into the corresponding *Me*$_2$ ester, b.p. 178—180°/3 mm. H. W.

Normal and *ψ*-esters of *o*-benzoylbenzoic acid type. M. S. Newman and C. D. McCleary (*J. Amer. Chem. Soc.*, 1941, **63**, 1537—1541).—*o*-C_6H_4Bz·CO_2H (**I**), m.p. 127·2—128·6°, *o*-C_6H_4Me·CO·C_6H_4·CO_2H-*o* (**II**), dimorphic, m.p. 130·2—132·2° and 113·8—115°, 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO·C_6H_4·CO_2H (**III**), m.p. 214—216·2°, 3 : 2 : 1- (**IV**), m.p. 172—173·5°, and 2 : 6 : 1-C_6H_3MeBz·CO_2H (**V**), m.p. 126—127°, and 3-*o'-toluoyl-o-toluic acid* (**VI**), m.p. 116·4—117·8°, with CH_2N_2–MeOH give normal Me esters, m.p. 51—51·8°, 41·5—43·5°, 86·8—88·2° (new), 104·6—105·6°, an oil, and m.p. 41·2—42·3° (new), respectively. The acid chlorides (prep. by $SOCl_2$) with MeOH–C_5H_5N give *ψ*-esters, *o*-C_6H_4<CO—CPh(OMe)>O and derivatives thereof, m.p. 81·4—82·4°, 69·6—70·6° (new), —, 124·4—125·4° (new), 120·6—121·6°, and 96·4—97·8°, respectively, but (**III**) gives the normal ester. With HCl–MeOH, (**I**), (**II**), (**III**), (**IV**), and (**VI**) give the normal esters, but (**V**) gives the *ψ*-ester. Mechanisms of the ester formations are discussed. Colours and rates of hydrolysis of the esters in conc. H_2SO_4 are not diagnostic of their nature. The normal esters of (**I**), (**II**), (**III**), and (**IV**) are stable in H_2SO_4, but all the other esters are hydrolysed. Structures of the acids are proved by decarboxylation in presence of a little Cu salt to the ketones. The following are recorded : 2 : 3'-*dimethylbenzophenone*, b.p. 228—231°/24 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 204—207°); 2-, m.p. 184—190°, and 3-*methylbenzophenone-2'* : 4'-*dinitrophenylhydrazone*, m.p. 220·4—221·4°. (**VI**) is prepared in 79·2% yield with 5·3% of 2-*o'-toluoyl-m-toluic acid*, m.p. 158—161·4°, from 3 : 2 : 1-$C_6H_3Me(CO)_2O$ and *o*-C_6H_4Me·MgBr in Et_2O–C_6H_6. M.p. are corr. R. S. C.

Reaction of β-benzilmonoxime with benzenesulphonyl chloride in presence of alkali. E. B. Ayres, M. Patterson, R. D. Bright, and C. R. Hauser (*J. Org. Chem.*, 1941, **6**, 804—809).—Evidence is presented in favour of the view that the derivative (**I**) obtained from β-benzilmonoxime (**II**) and $PhSO_2Cl$ in presence of alkali is the unrearranged derivative of (**II**) (cf. Werner *et al.*, A., 1905, i, 66). When dropped on red-hot Pt foil (**I**) decomposes vigorously with a pronounced odour of PhNC. At 120—130° PhNC cannot be detected and PhCN is obtained in 45% yield. When kept in KOH–EtOH at room temp. (**I**) gives <62% of the possible amount of PhCN and only 10% of PhNC. Under the conditions used PhNC is not transformed into PhCN. Similarly only a low yield of NH_2Ph is obtained from (**I**) and conc. H_2SO_4 at room temp. When kept in EtOH, H_2O, or dioxan containing

KOH (I) gives ~14% of the original (II). (I) has m.p. 122—123° (corr.; decomp.) (lit. m.p. 114°). H. W.

Coupling aryl radicals. 4 : 4′-Diaroyldiphenyls. R. C. Fuson and M. D. Armstrong (*J. Amer. Chem. Soc.*, 1941, **63**, 2650—2652).—2 : 4 : 6 : 1-$C_6H_2R_3$·CO·C_6H_4·Hal-*p* with Mg + MgI_2 in C_6H_6–Et_2O gives (*p*-2 : 4 : 6 : 1-$C_6H_2R_3$·CO·C_6H_4·)$_2$. The reaction mechanism is discussed in view of the facts that Mg does not cause coupling, free radicals are formed (red colours), and *o*- or *m*-halogen does not cause coupling. Friedel–Crafts reactions yield p- (I), m.p. 70—71°, m- (II), m.p. 86—87°, and o-*bromo*- (III), m.p. 113—115°, and p-*chloro-benzoylmesitylene*, m.p. 68—69·5°, p-*bromobenzoyltriethyl*-, b.p. 170—185°/7 mm., and -iso*propyl-benzene*, m.p. 99—99·5°. The coupling reaction gives 4 : 4′-*di*-2″ : 4″ : 6″-*tri-methyl*- (IV), m.p. 221—222°, -*ethyl*-, m.p. 148—149°, and iso*propyl-benzoyldiphenyl*, m.p. 190—191°. *p*-C_6H_4Cl·COPh or (II) does not react with Mg + MgI_2, and (III) gives 2 : 4 : 6 : 1-$C_6H_2Me_3$·COPh, b.p. 135—140°/4 mm. [$(NO_2)_3$-derivative, m.p. 202—204°]. Treatment of (I) with Mg + MgI_2 and then with Ac_2O gives a small amount of a *substance*, $C_{26}H_{38}O_3$, m.p. 190—191°. The structure of (IV) is proved by hydrolysis by syrupy H_3PO_4 to (*p*-CO_2H·C_6H_4)$_2$ and a hydrocarbon. Attempts to prepare (IV) from (*p*-COCl·C_6H_4)$_2$ and *s*-$C_6H_3Me_3$ failed. R. S. C.

Fluorenone-2 : 3-dicarboxylic acid and anhydride. W. C. Lothrop and J. A. Coffman (*J. Amer. Chem. Soc.*, 1941, **63**, 2564—2567).—Prep. of γ-keto-γ-2- (Koelsch, A., 1933, 1284) gives also 3% of γ-*keto*-γ-3-*fluorenyl*-n-*butyric acid*, m.p. 162—164°, oxidised by $Na_2Cr_2O_7$–AcOH to γ-*keto*-γ-3-*fluorenonyl*-n-*butyric acid* (60%), m.p. 178—180° (decomp.), and thence by $KMnO_4$ to fluorenone-3-carboxylic acid, m.p. 284—285°. 3′-Keto-3′ : 4′ : 5′ : 6′-tetrahydrobenz-1′ : 2′-2 : 3-fluorene (I) (*loc. cit.*; prep. in 91% yield from γ-2-fluorenyl-*n*-butyric acid), m.p. 149—150°, resists oxidation or gives tars with many reagents and with aq. alkaline $KMnO_4$ at 80—90° gives >13% of *fluorenone*-2 : 3-*dicarboxylic acid* (II), m.p. 250—275° (loss of H_2O) (*Me*$_2$, m.p. 131—133°, and *Et*$_2$ ester, m.p. 161—162°). Oxidation of the 9-*CHPh*· derivative, m.p. 234—235°, of (I) and of 8 : 9 : 8′ : 9′-*tetrahydro*-6 : 6′-*di*(*benzfluorenyl*) [obtained by pinacol-reduction of (I)], m.p. 193—195°, also gave poor results. *o*-*p*′-$C_6H_4Me·SO_2·NH·C_6H_4$·COCl and *o*-xylene give 2-p-*toluenesulphonamido*-3′ : 4′-*dimethyl*-, m.p. 132—133° (*Me* derivative, m.p. 118—120°), and thence successively 2′-*amino*-3 : 4-*dimethyl-benzophenone*, m.p. 82°, and (Ullmann) 2 : 3-dimethylfluorenone, m.p. 107—108° (lit. 109—110°), reduced by HI–AcOH to 2 : 3-dimethylfluorene and converted by boiling HNO_3–H_2O into 3-*methylfluorenone*-2-*carboxylic acid* (III) (74%), m.p. 307—309° (*Me* ester, m.p. 175—176°). With Cu carbonate in quinoline at 210°, (III) gives 3-methylfluorenone, m.p. 67—68° (lit. 66·5°), with alkaline $KMnO_4$ at 70° gives 66% of (II), and with HI-red P gives 3-*methylfluorene*-2-*carboxylic acid* (85%), m.p. 261—263° (*Me* ester, m.p. 119—120°). The *anhydride* (IV), m.p. 322—323°, of (II), obtained by boiling Ac_2O, shows no Mills–Nixon effect: its reaction with N-$NaHCO_3$ is as fast as that of *o*-$C_6H_4(CO)_2O$; with C_6H_6–$AlCl_3$ it gives 2-*benzoylfluorenone*-3-*carboxylic acid*, m.p. 247—250° (*Me* ester, m.p. 185—187°), decarboxylated to 2-benzoylfluorenone; with NH_2Ph it gives the *anil*, m.p. 310—312°, and with PhOH or *m*-$C_6H_4(OH)_2$ gives products similar to phenolphthalein and fluorescein but having enhanced colours. Fluorene-2 : 3-dicarboxylic acid or anhydride cannot be obtained from (II) or (IV) by HI–red P or Na–Hg. R. S. C.

Synthesis of 4-ketohexahydroindane. W. E. Bachmann and W. S. Struve (*J. Amer. Chem. Soc.*, 1941, **63**, 2589—2591).—Addition of Br·$[CH_2]_3$·CO_2Et to the K derivative of Et *cyclo*pentanone-2-carboxylate in PhMe and then boiling gives *Et* γ-2-*keto*-1-*carbethoxy*cyclo*pentyl*-n-*butyrate* (79%), b.p. 140—145°/0·4 mm., converted by boiling, conc. HCl into γ-2-*keto*-cyclo*pentyl*-n-*butyric acid* (53%), b.p. 153—156°/0·2 mm., the *Me* ester, b.p. 143—146°/14 mm., of which with a trace of 45% aq. KOH in liquid HCN gives *Me* γ-2-*hydroxy*-2-*cyano*-cyclo*pentyl*-n-*butyrate* (I), b.p. 163—165°/3 mm. When this is dehydrated by $SOCl_2$–C_5H_5N, first at <0° and then at 100°, erratic yields (up to 70%) of Me γ-2-carboxy-Δ^1-*cyclo*-pentenyl-*n*-butyrate, b.p. 130—133°/3 mm., are obtained, but at <0° and later room temp. 53% of the Δ^2-monoester (II), b.p. 130—135°/3 mm., is formed. Hydrolysis of (I) by boiling, conc. HCl gives the Δ^1-*acid* (III) (17%), m.p. 121—122° (*Me*$_2$ ester, b.p. 173—176°/26 mm.), and of (II) by NaOH gives the Δ^2-*acid* (IV) (17% over-all), m.p. 137·5—138·5° (*Me*$_2$ ester, b.p. 137—139°/3 mm.). Hot Ac_2O converts (IV) into 4-keto-Δ^2-hexahydroindene (V), b.p. 120—126°/20 mm. (*semicarbazone*, m.p. 236—237°; *oxime*, *forms*, m.p. 128—129° and 136·5—138°). Hydrogenation (PtO_2; EtOH) of (III) or (IV) gives γ-2-*carboxy*cyclo*pentyl*-n-*butyric acid*, m.p. 81—83° (80—82°). The derived (? mixed *cis–trans*-)*Me*$_2$ esters (obtained by hydrogenation), b.p. 133—137°/3 mm., are cyclised by NaOMe–C_6H_6 to 4-ketohexahydroindane (80%), b.p. 115—119°/3 mm., also obtained by hydrogenation (Pd–C–EtOH) of (V) and identical with the product (? equilibrium mixture) of Hückel *et al.* (A., 1937, II, 22). R. S. C.

Raman spectra evidence for hindrance of resonance by *o*-substitution.—See A., 1942; I, 83.

Mechanism of the addition of hydrogen cyanide to *p*-benzoquinone. C. F. H. Allen and C. V. Wilson (*J. Amer. Chem. Soc.*, 1941, **63**, 1756—1757).—The abnormal formation of 2 : 3-dicyanoquinol from *p*-O:C_6H_4:O by HCN (only at 20—30°) is explained by noting that the primary product, 2-cyano-*p*-benzoquinone, contains CH:C·C:N which is more reactive than C:C·C:O. R. S. C.

Anthraquinone-2-sulphonalkylanilides. C. A. Buehler and W. J. Williams (*J. Amer. Chem. Soc.*, 1941, **63**, 2852).—Anthraquinone-2-sulphonanilide (modified prep.) with KOH–EtOH–PhMe gives the solid K salt, which with boiling RHal–H_2O gives *anthraquinone*-2-*sulphon*-N-*ethyl*-, m.p. 192—193°, -n-, m.p. 206·5°, and -iso-*propyl*-, m.p. 256°, -n-, m.p. 172·5—173°, -iso-, m.p. 210·5—211°, and -sec.-*butyl*-, m.p. 214·5—215·5°, -n-, m.p. 153—154°, and -iso-*amyl*-, m.p. 172—173°, -*hexyl*-, m.p. 145—146°, -*heptyl*-, m.p. 141·0—141·5°, -*benzyl*-, m.p. 194—195°, and -*allyl-anilide*, m.p. 194·0—194·5°. M.p. are corr. R. S. C.

Isologues of 9 : 10-dimethyl-1 : 2-benzanthracene containing sulphur and selenium.—See A., 1942, II, 112.

IV.—STEROLS AND STEROID SAPOGENINS.

Autoxidation of sterols in colloidal aqueous solution. Nature of products formed from cholesterol. S. Bergström and O. Wintersteiner (*J. Biol. Chem.*, 1941, **141**, 597—610; cf. A., 1940, II, 139).—Cholesterol (I), aërated at 85° in colloidal aq. solution, is mainly transformed into a mixture containing 7-ketocholesterol (main product), 7-keto-Δ$^{3:5}$-cholestadiene, 7(α)-hydroxycholesterol, and (?) Δ^6-*cholestene*-3 : 5-*diol*, m.p. 139—140°, $[\alpha]_D^{24}$ −134° in $CHCl_3$ (*monobenzoate*, m.p. 117°; 3 : 5-*dinitrobenzoate*, m.p. 163—164°); the last-named is a rearrangement product of 7(β)-hydroxycholesterol, formed during separation with Girard's reagent. Thus, position 7 in (I) is easily attacked by mol. O_2, whereas the 3-OH is not involved. A. T. P.

Steroids and sex hormones. LXXII. Preparation of Δ^2-2-formylcholestene. P. A. Plattner and L. M. Jampolsky (*Helv. Chim. Acta*, 1941, **24**, 1459—1464; cf. A., 1939, II, 76).—Freshly prepared cholestenoneoxalic acid (*loc. cit.*) has $[\alpha]_D$ −204° in $CHCl_3$; the val. gradually becomes positive even in the absence of light and O_2. The pure material is necessary for the hydrogenation (Pd-sponge in EtOH at 20°) to the tetrahydrolactone (I), m.p. 230° (decomp.), $[\alpha]_D$ −48° in $CHCl_3$. Distillation of (I) under diminished pressure gives Δ^2-2-*formylcholestene* (II), m.p. 130—132°, $[\alpha]_D$ +74·8°±7° in $CHCl_3$ [*oxime* (II), m.p. 163—164°, $[\alpha]_D$ +52·3°±3° in $CHCl_3$, and its *acetate*, m.p. 122—123°]. The absorption spectrum of (II) indicates that the double linking is in conjugation with CO. (III) is converted by NaOAc and boiling Ac_2O into 2-*cyano*-Δ^2-*cholestene*, m.p. 125·5—127·5°, $[\alpha]_D$ +72·2°(±4°) in $CHCl_3$. Hydrogenation (Pt in EtOH at 21°) of (II) gives 2-*hydroxymethylcholestane*, m.p. 124—126°, $[\alpha]_D$ +19·5° in $CHCl_3$. M.p. are corr. H. W.

[Relation between] structure and absorption spectra. II. 3-Acetoxy-Δ^5-(6)-*nor*cholestene-7-carboxylic acid. R. B. Woodward and A. F. Clifford (*J. Amer. Chem. Soc.*, 1941, **63**, 2727—2729).—The structure, 3-*acetoxy*-Δ^5-(6)-nor*cholestene*-7-*carboxylic acid*, previously (A., 1941, II, 197) suggests for the compound (I), new m.p. 232—232·5° (corr.), designated "7-hydroxy-6-keto-3-acetoxy-Δ^4-cholestene" by Heilbron *et al.* (A., 1938, II, 103), is confirmed. Prep. of (I) and its precursor, the Br_2-ketone, is improved. With aq. K_2CO_3, (I) gives a K salt. It has only one absorption max. (<230 mμ). With boiling EtOH and a little H_2SO_4, (I) gives the Et ester,

previously (*loc. cit.*) designated the Et ether (acetate, m.p. 119·5—121°), and with boiling KOH–EtOH–H_2O gives the 3-OH-acid [the " diol " (*loc. cit.*)], which, when distilled at ~320°/25 mm., gives the known $\Delta^{3:5}$-(6)-*nor*cholestadiene. Analogy for formation of (I) is provided by Wallach (A., 1918, i, 442). R. S. C.

Ethers and esters of 3-hydroxy-Δ^5-cholenic acid. B. Riegel, J. A. Vanderpool, and M. F. W. Dunker (*J. Amer. Chem. Soc.*, 1941, **63**, 1630—1632).—Me 3-hydroxy-Δ^5-cholenate in C_5H_5N gives the 3-p-*toluenesulphonate*, m.p. 120—120·6° (decomp.), which with $CH_2Ph{\cdot}OH$ at 100° gives *CH_2Ph 3-benzyloxy-Δ^5-cholenate* (I), dimorphic, m.p. 87—88° and 108·5—109·5°, $[\alpha]_D^{20}$ −23·9°±0·2° in $CHCl_3$, hydrolysed to *3-benzyloxy-Δ^5-cholenic acid*, m.p. 166—168° [*Me* ester (II), m.p. 99—100·5°]. 3-Hydroxy-Δ^5-cholenic acid (purification described), $CH_2Ph{\cdot}OH$, and a little H_2SO_4 at 100° give *CH_2Ph 3-hydroxy-Δ^5-cholenate*, m.p. 81·5—82·5°, and (I). No CH_2Ph ether could be obtained from (II). CPh_3Cl and (II) in C_5H_5N at 100° give *Me 3-triphenylmethoxy-Δ^5-cholenate*, m.p. 147·5—149°, converted by boiling AcOH into the 3-OAc-compound. M.p. are corr. R. S. C.

Introduction of double linkings into bile acids and sterols. III. Preparation of $\Delta^{5:7}$-choladienic acid. E. Dane and H. Wulle (*Z. physiol. Chem.*, 1940, **267**, 1—6; cf. A., 1937, II, 417).—6-Bromo-7-ketocholanic acid [obtained in improved yield (cf. A., 1932, 1131) by treatment of 7-ketocholanic acid in Br–AcOH with HBr; yields, when boiled with 0·5N-NaOH for 1 hr., *6-hydroxy-7-ketocholanic acid*, m.p. 169°, which is oxidised (CrO_3–AcOH) to thilobilianic acid] with $AgNO_3$–C_5H_5N is debrominated to *Δ^5-7-ketocholenic acid*, m.p. 164—165° (absorption max. at 239 mμ, indicates double linking between $C_{(5)}$ and $C_{(6)}$ in conjugation with CO group), the *Me* ester, m.p. 73°, of which is reduced by $Al(OPr^\beta)_3$ in $Pr^\beta OH$ to *$\Delta^{5:7}$-choladienic acid*, m.p. 160—169° (*Me* ester, m.p. 102—103°), hydrogenated to *allo*cholanic acid. F. O. H.

Bile acids. LXI. M. Schenck (*Z. physiol. Chem.*, 1940, **265**, 88—93).—Oxidation of bilianic acid oxime lactam with CrO_3 under strictly defined conditions leads to the blue NO-compound, $C_{24}H_{34}O_8N_2$, decomp. 230—232°, also obtained by use of HNO_3 and characterised by transformation by an excess of alkali into the ketolactamtricarboxylic acid, $C_{24}H_{35}O_8N$, " small crystals," decomp. ~200°, or needles, decomp. ~260°. The mono-oxime of bilianic acid (I) is oxidised by CrO_3 to a blue product, $C_{24}H_{33}O_8N$, decomp. ~236—238°, identical with that obtained by use of HNO_3, and immediately converted by ~5% NaOH into (I). H. W.

Bile acids. LXIII. M. Schenck (*Z. physiol. Chem.*, 1940, **267**, 7—13).—Bilianic acid oxime lactam (I) is oxidised ($KMnO_4$–50% H_2SO_4) to a NO_2-compound, $C_{24}H_{34}O_9N_2$, decomp. 250—252° [reduced to (I) by Zn–AcOH], which with 10% NaOH yields a ketolactamtricarboxylic acid, $C_{24}H_{35}O_8N$, and with HNO_3 (*d* 1·4) a nitroketolactamtricarboxylic acid, $C_{24}H_{34}O_{10}N_2$. These reactions are analogous to those occurring with 7-nitrodeoxybilienic acid, viz., $\cdot C(NO_2){:}C{:} \rightarrow \cdot C(:NOH){\cdot}CH{:}$, $\cdot C(NO_2){:}C{:} \rightarrow \cdot C(OH){:}C{:} \rightarrow \cdot CO{\cdot}CH{:}$, and $\cdot CH_2{\cdot}C(NO_2){:}C{:} \rightarrow \cdot C(:NO_2H){\cdot}CO{\cdot}CH{:}$ for the action of Zn–AcOH, 10% NaOH, and HNO_3, respectively. F. O. H.

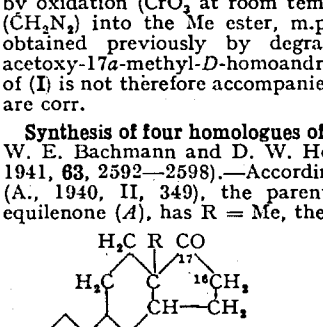
Steroid α-ketols. I. Partial synthesis of 16-ketotestosterone acetate. F. H. Stodola and E. C. Kendall (*J. Org. Chem.*, 1941, **6**, 837—840).—Androstene-3 : 17-dione 3-enol Et ether in boiling MeOH containing NaOMe is transformed by gradual addition of PhCHO into the 16-*CHPh*: compound, m.p. 181—186° after softening at 177°, transformed by reduction with $Al(OPr^\beta)_3$ in boiling C_6H_6 followed by treatment with warm AcOH and then with Ac_2O and C_5H_5N at 60° into *16-benzylidenetestosterone acetate*, m.p. 178—179°, occasionally with re-solidification and re-melting at 197—198°. This is transformed by OsO_4 in CCl_4 followed by reduction with Zn dust and AcOH at 45—50° and cleavage of the glycol by HIO_4 into *16-ketotestosterone acetate* (I), m.p. 194—195°, $[\alpha]_{4361}^{25}$ −56° in 95% EtOH. (Difficulty is experienced since residual traces of Os appear to enhance the activity of HIO_4 to such an extent that other parts of the mol. are attacked.) The physiological properties of the amorphous fraction of the extract of the adrenal cortex are not due to (I). H. W.

Steroids. VI. New method of preparing 6(α)-acetoxyprogesterone. M. Ehrenstein and T. O. Stevens (*J. Org. Chem.*, 1941, **6**, 908—919).—Oxidation of pregnenolone by BzO_2H in $CHCl_3$ at room temp. yields 5 : 6-α-oxidopregnan-3(β)-ol-20-one (I), m.p. 180—184°, becoming clear at 187°, $[\alpha]_D^{24}$ +1·0° in $COMe_2$, the mother-liquors from which when treated with 10% H_2SO_4 afford pregnane-3(β) : 5 : 6-triol-20-one, m.p. 250—253°. (I) is converted by boiling Ac_2O into the acetate, m.p. 167—168°. Glacial AcOH at ~120° converts (I) into *pregnane-3(β) : 5 : 6(trans)-triol-20-one 6-monoacetate* (II), m.p. 247—248·5°, $[\alpha]_D^{23}$ +8·0° in $COMe_2$, and the 3 : 6-*diacetate* (III), m.p. 217—219°. (III) is also obtained by acetylation of (II) by boiling Ac_2O and (II) by partial hydrolysis of (III) by 0·1N-KOH–EtOH at room temp. Oxidation (CrO_3 in AcOH) of (II) leads to pregnane-5 : 6-(*trans*)-diol-3 : 20-dione 6-monoacetate, plates, m.p. 218—221°, or needles, m.p. 215—218°, $[\alpha]_D^{24}$ +20·5° in $COMe_2$, converted by HCl in dry $CHCl_3$ into Δ^4-pregnen-6-(α)-ol-3 : 20-dione acetate [6(α)-acetoxyprogesterone], $[\alpha]_D^{22.5}$ +106·7° in abs. EtOH, +104·0° in $COMe_2$, which could not be caused to crystallise. (I) is oxidised by CrO_3 or $KMnO_4$ to pregnan-5-ol-3 : 6 : 20-trione, m.p. 262—264° (decomp.). H. W.

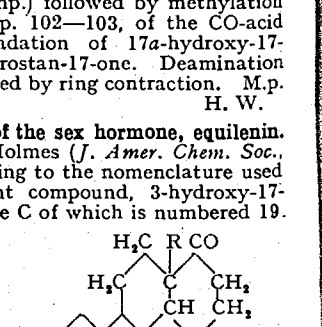
Steroid α-ketols. II. New partial synthesis of Δ^5-androstene-3 : 16 : 17-triol, an intermediate in the preparation of 16-hydroxytestosterone. F. H. Stodola, E. C. Kendall, and B. F. McKenzie (*J. Org. Chem.*, 1941, **6**, 841—844).—Gradual addition of $C_5H_{11}{\cdot}O{\cdot}NO$ to a well-stirred solution of dehydro*iso*androsterone and K in $Bu^\gamma OH$ under N_2 at room temp. affords *oximinodehydroisoandrosterone*, m.p. 248—249° (decomp.) after softening at 240° (3-*acetate*, m.p. 183—184°). This is reduced by Zn dust and AcOH at 40—45° to a mixture (I) of α-ketols, transformed by H_2–Raney Ni in EtOH into Δ^5-androstene-3 : 16 : 17-triol, m.p. 273—275° (cf. Butenandt *et al.*, A., 1939, II, 165). Acetylation (Ac_2O–C_5H_5N at room temp.) of (I) gives either 3 : 16-diacetoxy-Δ^5-androsten-17-one or 3 : 17-diacetoxy-Δ^5-androsten-16-one, m.p. 124—125° (lit. m.p. 123°), reduced (H_2–Raney Ni) to Δ^5-androstene 3 : 16 : 17-triol triacetate, m.p. 214—215° (Butenandt records m.p. 224—226°). By the use of this method it is now possible to obtain 16-hydroxytestosterone in a yield ten times that previously reported (*loc. cit.*). H. W.

Steroids and sex hormones. LXXI. 17-Amino-3 : 17*a*-dihydroxy-17*a*-methyl-*D*-homoandrostane and the products of its transformations. L. Ruzicka and H. F. Meldahl [with in part, F. Muhr] (*Helv. Chim. Acta*, 1941, **24**, 1321—1328; cf. A., 1939, II, 327).—Δ^5-3 : 17*a*-Dihydroxy-17*a*-methyl-*D*-homoandrosten-17-one is converted by NH_2OH,HCl–NaOAc in boiling MeOH–dioxan into its *oxime*, m.p. 263—265° (decomp.), readily reduced (H_2–PtO_2 in AcOH–EtOH) to 17-*amino*-3 : 17a-*dihydroxy*-17a-*methyl*-D-*homoandrostane* (I), m.p. 263—266° (decomp.). (I) is readily de-aminated by $NaNO_2$ and AcOH to 3-*hydroxy*-17 : 17a-*oxido*-17a-*methyl*-D-*homoandrostane* (II), m.p. 163—165°, which retains solvent MeOH with great obstinacy and is analysed as the *acetate* (III), m.p. 158—160°. (II) or (III) does not react with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, NH_2OH, or Girard's reagent *T* and the presence of the oxide ring is established by the production of 3 : 17 : 17*a*-trihydroxy-17*a*-methyl-*D*-homoandrostane 3 : 17-diacetate, m.p. 256—258°, from (III) and boiling AcOH; it is hydrolysed to the triol, m.p. 292—294°. (III) is converted by oxidation (CrO_3 at room temp.) followed by methylation (CH_2N_2) into the Me ester, m.p. 102—103, of the CO-acid obtained previously by degradation of 17*a*-hydroxy-17-acetoxy-17*a*-methyl-*D*-homoandrostan-17-one. Deamination of (I) is not therefore accompanied by ring contraction. M.p. are corr. H. W.

Synthesis of four homologues of the sex hormone, equilenin. W. E. Bachmann and D. W. Holmes (*J. Amer. Chem. Soc.*, 1941, **63**, 2592—2598).—According to the nomenclature used (A., 1940, II, 349), the parent compound, 3-hydroxy-17-equilenone (*A*), has R = Me, the C of which is numbered 19.



(*A*.)



(VII.) and (VIII.)

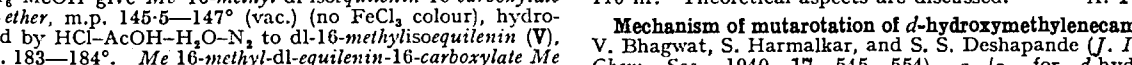
Thus, *e.g.*, the 19-Et derivative is (*A*; R = Pr). Me 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene-2-carboxylate (I) (A., 1940, II, 225), NaOMe, and $Pr^\alpha I$ in MeOH–C_6H_6 give the 2-*Pr^α* compound (86%), m.p. 144—145°, converted by Zn–$CH_2Br{\cdot}CO_2Me$ (details of this and other preps. as

loc. cit.) into *Me*$_2$ 1-*hydroxy*-7-*methoxy*-2-n-*propyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylate*-1-*acetate* (86%), m.p. 112·5—113·5°. Successive conversion into the chloride by $SOCl_2$–C_5H_5N, hydrolysis and removal of HCl by KOH–EtOH, and reduction by 2% Na–Hg in H_2O then gives impure α-, m.p. 228—230°, and (pure) β-7-*methoxy*-2-*carboxy*-2-n-*propyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-1-*acetic acid* (31—37%), m.p. 253—255°. The derived α-, m.p. 109·5—111°, and β-*Me*$_2$ ester, m.p. 118·5—119·5°, with boiling NaOH–aq. EtOH give α- (crude), m.p. 110—118°, and β-7-*methoxy*-2-*carbomethoxy*-2-n-*propyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-1-*acetic acid*, m.p. 116·5—117·5°, the acid chlorides of which with CH_2N_2–KOH–Et_2O and then Ag_2O–MeOH give *Me* β-7-*methoxy*-2-*carbomethoxy*-2-n-*propyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylpropionate*, α- (40—50%), m.p. 91—94°, and β-*form* (86%), m.p. 86—87°. These esters are cyclised by NaOMe–C_6H_6 to *Me* 3-*methoxy*-19-*ethyl*-17-*equilenone*-16-*carboxylate*, α- (84%), m.p. 135—136° (vac.), and β-*form* (70—95%), m.p. 172·5—173·5° (vac.), converted by boiling HCl–AcOH–H_2O–N_2 in 0·5 hr. into 3-*methoxy*-, α- (77%), m.p. 103·5—104·5° (vac.), and β-*form* (88%), m.p. 148—149·5° (vac.), or in 11 hr. into 3-*hydroxy*-19-*ethyl*-17-*equilenone* (*A*; R = Pr^n), α- (II) (83%), m.p. 153—154° (vac.), and β-*form* (III) (83%), m.p. 236—237° (vac.). Bu^{n}I–NaOMe–MeOH–C_6H_6 converts (I) into *Me* 1-*keto*-7-*methoxy*-2-n-*butyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylate* (89%), m.p. 111—112°, and then as above gives *Me*$_2$ 1-*hydroxy*-7-*methoxy*-2-n-*butyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylate*-1-*acetate*, m.p. 84·5—86° after slight softening, 7-*methoxy*-2-*carboxy*-, α-, m.p. 190·5—191·5° (*Me*$_2$ ester, m.p. 75·5—77°), and β-*form*, m.p. 224—226° (*Me*$_2$ ester, m.p. 90—91°), and 7-*methoxy*-2-*carbomethoxy*-2-n-*butyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-1-*acetic acid*, α-, m.p. 125—127°, and β-*form*, m.p. 193—194·5°, *Me* β-7-*methoxy*-2-*carbomethoxy*-2-n-*butyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylpropionate*, α-, an oil, and β-*form*, m.p. 95·5—96·5°, *Me* 3-*methoxy*-19-n-*propyl*-17-*equilenone*-16-*carboxylate*, α-, m.p. 115·5—116·5°, and β-*form*, m.p. 153—154° (vac.), and 3-*hydroxy*-19-n-*propyl*-17-*equilenone* (*A*; R = Bu^n), α-, an oil [*Me ether*, *forms*, m.p. 93—94° (vac.) and 104—105° (vac.)], and β-*form* (IV), m.p. 191—192° (vac.) (*Me ether*, m.p. 141—142°). Me *di-iso*equilenin-16-carboxylate Me ether (*loc. cit.*), MeI, and NaOMe in boiling C_6H_6–MeOH give *Me* 16-*methyl*-dl-iso*equilenin*-16-*carboxylate Me ether*, m.p. 145·5—147° (vac.) (no $FeCl_3$ colour), hydrolysed by HCl–AcOH–H_2O–N_2 to dl-16-*methyliso*equilenin (V), m.p. 183—184°. *Me* 16-*methyl*-dl-*equilenin*-16-*carboxylate Me ether*, m.p. 163—164° (vac.), and dl-16-*methylequilenin* (VI), m.p. 261·5—263° (vac.), are similarly obtained. β-7-*Methoxy*-2-*carbomethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylpropionic acid* (prep. from the Me_2 ester as above), α-, m.p. 114—119°, and β-*form*, m.p. 184—185°, gives (CH_2N_2 etc.) *Me* γ-7-*methoxy*-2-*carbomethoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthryl*-n-*butyrate*, α-, m.p. 66—67°, and β-*form*, m.p. 119—120·5°, cyclised (NaOMe–C_6H_6) to *Me* dl-D-*homo*iso*equilenin*-, m.p. 133—135° (vac.) (reddish-purple $FeCl_3$ colour given only slowly), and *Me* dl-D-*homoequilenin*-17-*carboxylate*, m.p. 158·5—160° (vac.) (light violet $FeCl_3$ colour given only slowly), and thence dl-D-*homoiso*equilenin (VII), m.p. 239—240° (vac.) (*Me ether*, m.p. 125—126°), and dl-D-*homoequilenin* (VIII), m.p. 232—233° (vac.) [Me ether, m.p. 213—214° (vac.), identical with the compound of Burnop *et al.* (A., 1940, II, 282). Doses for œstrogenic activity equal to that of 1 μg. of œstrone are (II) 250, (III) 25, (VIII) 100, and *dl*-equilenin ~60 μg. (IV), (V), and (VII) are inactive in 1-mg. doses. (VI) is inactive in 0·5- but has some activity in 1-mg. doses. The α-forms of the 16-CO_2Me-derivatives of (*A*) give immediate deep blue colours with $FeCl_3$–EtOH, but the β-forms give a faint colour developing slowly or none at all; for all known pairs (R = Me, Et, and Pr) the β-form of (*A*) is the more active. R. S. C.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Camphor, borneol, and allied substances. S. Yamada (*Bull. Chem. Soc. Japan*, 1941, **16**, 187—196).—Borneol (I) passed (at 400°) over Cu (*A*), prepared from CuO [NaOH–$Cu(NO_3)_2$] gives camphor (II) (quant.), whilst Cu (*B*), from CuO [aq. NH_3–$Cu(NO_3)_2$] or Cu from CuO [heat, $Cu(NO_3)_2$] yields (II) + camphene (III) (4 : 1 or 87 : 13, respectively). *iso*Borneol (IV) with Cu (*A*) at 150° or 300° yields (II); Cu (*B*) affords at 150°, (III), or at 300°, (II) + (III) (24 : 76). (II) is reduced (H_2–reduced Ni) at 180°, or 140—160°, or 170—190°, at 23—85 atm., to (I), $[\alpha]_D^{11}$ +38·1° in EtOH (Mg phthalate, m.p. 103—104°. $[\alpha]_D^{15}$ +31·9° in EtOH) + (IV), $[\alpha]_D^{7}$ −34·42° in EtOH (Mg phthalate, m.p. 95—97°, $[\alpha]_D^{15}$ −29·46° in EtOH), in approx. equal proportions, with slight increase in (IV) at higher temp.; at >200°, some *iso*camphane is found. When *cyclo*hexane, AcOH, EtOH, or C_5H_5N is used as solvent, proportions formed of (I) : (IV) are 23 : 77, 12 : 88, 37 : 63, or 36 : 64, respectively. Dimethylcamphor and Na–EtOH or H_2–Ni at 220—230°/60 atm. (19% yield) afford dimethyl-borneol, m.p. 57°, $[\alpha]_D^{20}$ +50·72° in EtOH (phenylurethane, m.p. 112—113°; *p*-nitrobenzoate, m.p. 115—115·8°; H phthalate, m.p. 177—178°; Mg phthalate, m.p. 175—176·2°) + *iso*borneol (V), m.p. 47—49°, $[\alpha]_D^{15}$ +36·47° in EtOH (phenylurethane, m.p. 116—117°; *p*-nitrobenzoate, m.p. 114·5—115°; H phthalate, m.p. 173—174°; Mg phthalate, m.p. 180—182°) [88 : 12 or 85 : 15, respectively; use of AcOH as solvent in the catalytic reduction does not alter the result appreciably, but EtOH increases the yield of (V) to give a ratio of 66 : 34]. (IV) and H_2 (reduced Ni) at 130—150° or 140—165°/50 atm. give (I) in 16 or 51% yield, respectively. Only 1% of (I) is converted into (IV) with H_2 (reduced Ni) at 170—190°/70 atm.; (I) or (IV) in EtOH similarly gives ~10% conversion. (I) or (IV) and H_2SO_4,$3H_2O$ at 140—145° afford 63% or 56% of camphene, respectively, together with some ether. The rotatory powers of camphenes formed vary with the time and temp. of reaction, and kind, concn., and amount of acid used. Bornyl acetate and H_2SO_4,$3H_2O$ at 140—145° give *iso*bornyl acetate + camphene. Dimethylborneol and H_2SO_4,$3H_2O$ at 140—141° yield a mixture (VI), b.p. 48—82°/5 mm., of hydrocarbons of both camphene and bornylene forms, dehydrated by P_2O_5 to a single hydrocarbon, b.p. 192—193°. (VI) and O_3–$CHCl_3$ yield a (?) *monoketone*, b.p. 72—73°/6 mm. (*semicarbazone*, m.p. 243·6—243·9°; Na–EtOH gives an alcohol, b.p. 82—86°/5 mm.), and a *diketone* (VII), b.p. 120—123°/6 mm. (VII) with HNO_3 (*d* 1·29) or by distillation (decomp.) gives camphoric acid, and (VII)–Na–EtOH afford glycol derivatives. (VI) and O_3–C_6H_6 give a diketone, b.p. 112—114°/4 mm. Camphene and 50% H_2SO_4–AcOH yield (IV) +10% of (I); [α] of (IV) decreases gradually to zero during 110 hr. Theoretical aspects are discussed. A. T. P.

Mechanism of mutarotation of *d*-hydroxymethylenecamphor. V. Bhagwat, S. Harmalkar, and S. S. Deshapande (*J. Indian Chem. Soc.*, 1940, **17**, 545—554).—α_∞/α_0 for *d*-hydroxymethylenecamphor (I) in EtOH is independent of initial concn. The mutarotation with or without HCl follows a first-order law. Titration with NaOH, or of the pptd. Cu derivative with $Na_2S_2O_3$, shows that (I) contains ≮80% of enol form. The amount of enol decreases to a const. val.; the rate of decrease in presence of HCl does not follow a first-order law ($Na_2S_2O_3$ titration), but if the mechanism



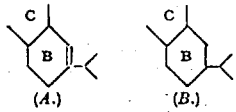
is assumed, the first reaction does. A. Li.

Absorption spectra of terpenoid compounds. I. "*iso*-Thujone." A. E. Gillam and T. F. West (*J.C.S.*, 1941, 811—814).—The location of the absorption band at 2375 A. classifies *iso*thujone (I) as a disubstituted αβ-unsaturated ketone, whereas the generally accepted formula involves tri-substitution of the chromophoric grouping. Hence either (I) is exceptional among αβ-unsaturated ketones or the accepted formula is incorrect. The *l*-form of (I) derived from *d*-sabinol shows the usual two max. F. R. S.

Effect of molecular environment on absorption spectra of αβ-unsaturated ketones.—See A., 1941, I, 81.

Diterpenes. LI. Dihydroabietic acids and two isomeric dihydroxydihydroabietic acids. L. Ruzicka and S. Kaufmann [with E. Schwob] (*Helv. Chim. Acta*, 1941, **24**, 1389—1395).—Hydrogenation (Pd–$CaCO_3$ in MeOH) of abietic acid, m.p. 158—159°, $[\alpha]_D$ −72° in EtOH, ceases after absorption of ~1 mol. of H_2 but homogeneous products cannot be isolated from the mixture by fractional crystallisation from $COMe_2$. Treatment of a fraction of m.p. ~180°, $[\alpha]_D$ −5° in $COMe_2$ (which does not alter on further crystallisation), with $KMnO_4$ does not yield cryst. oxidation products but establishes the presence of much tetrahydroabietic acid, m.p. 179—181°, $[\alpha]_D$ +6·2° in EtOH, which does not yield a cryst. Me ester and does not give a yellow colour with $C(NO_2)_4$. Similar

oxidation of a fraction of lower m.p. (120—125°) leads to the isolation of an apparently homogeneous *dihydroxydihydroabietic acid* (I), m.p. 226—227°, $[\alpha]_D$ −14° in EtOH (*Me* ester, m.p. 162—163°, $[\alpha]_D$ −18° in EtOH; *monoacetate*, m.p. 200—201°), which does not give cryst. degradation products when treated with $Pb(OAc)_4$ or CrO_3. Hydrogenation (PtO_2 in AcOH at 50°) of dihydroxyabietic acid gives a very hygroscopic *dihydroxydihydroabietic acid*, m.p. 225—226°, $[\alpha]_D$ −21° in EtOH (*Me* ester, m.p. 103—104°; *acetate*, m.p. 124—126°, and its *Me* ester, m.p. 168·5—169·5°), which is not identical with (I). Neither acid lactonises when boiled in PhMe. (I) is probably (*A*) or (*B*). This conclusion is valid only for the H_2-acid which is most readily attacked by $KMnO_4$; the isolation of a less readily oxidised *dihydroabietic acid*, m.p. 166—168°, has been effected. M.p. are corr. H. W.



(*A.*) (*B.*)

Diterpenes. LH. Quinone adduct and permanganate oxidation of *l*-pimaric acid. L. Ruzicka and S. Kaufmann (*Helv. Chim. Acta*, 1941, **24**, 1425—1434).—In consequence of the criticism of Sandemann (*Ber.*, 1941, **74**, 104) evidence is adduced to show that " original pine resin acid " (I) and *l*-pimaric acid (II) may give different results. Wienhaus and Sandemann (A., 1936, 1385) describe an adduct, m.p. 214°, $[\alpha]_D$ −148° in $CHCl_3$, from (I), $[\alpha]_D$ −112° in $CHCl_3$, and *p*-O:C_6H_4:O. Under like conditions (II) is quantitatively converted into the *adduct* (III), $C_{21}H_{34}O_4$, m.p. 190°, $[\alpha]_D$ −163° in $CHCl_3$. The absorption spectrum of (III) has max. at 230, 295, and 380 mμ. Hydrogenation (PtO_2 in EtOAc) of (III) gives a *compound* (IV), $C_{21}H_{38}O_4$, m.p. 260—264° after softening, in which 1 CO has been reduced to CH(OH) since (IV) yields an *acetate*, m.p. 209—213°, with Ac_2O in C_5H_5N at room temp. Further hydrogenation (PtO_2 in AcOH at room temp.) leads to the *diol*, $C_{21}H_{40}O_4$, m.p. 202—205°, which does not give a colour with $C(NO_2)_4$ and is dehydrogenated by Se at 350° to retene. Oxidation of (II) by $KMnO_4$ under a combination of the conditions of Wienhaus (*loc. cit.*) and Ruzicka *et al.* (A., 1938, II, 287) gives the sparingly sol. $(OH)_2$-acid, m.p. 200—202° (non-cryst. Me ester), and, after methylation of the mother-liquors with CH_2N_2–Et_2O, the Me ester (V), m.p. 183°, $[\alpha]_D$ +13·5° in MeOH, of Wienhaus' oxidodihydroxy-acid. The more freely sol. isomeric $(OH)_2$-acid, m.p. 191—196°, could not be isolated. (V) is not identical with the *Me* ester, m.p. 174—176°, of the isomeric acid, $C_{20}H_{32}O_5$, from (II). It is therefore established that oxidation of (II) by $KMnO_4$ gives two isomeric $(OH)_2$-acids and two isomeric oxidodihydroxy-acids. (II) absorbs 2 O from *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_2H$ but the product decomposes rapidly and cannot be isolated pure. Dihydro-*l*-pimaric acid under similar conditions absorbs 1 O giving a *compound*, $C_{20}H_{32}O_3$, m.p. 133—135°, $[\alpha]_D$ −16·5° in EtOH, which does not give a yellow colour with $C(NO_2)_4$ and therefore represents an oxidodihydro-*l*-pimaric acid. M.p. are corr. H. W.

VI.—HETEROCYCLIC.

Tetrahydrofuran compounds. I. Cleavage by hydrogen halides. S. Fried and R. D. Kleene (*J. Amer., Chem. Soc.*, 1941, **63**, 2691).—The relative ease of fission of tetrahydrofuran or 2 : 5-dimethyltetrahydrofuran by HHal is HI > HBr > HCl ($ZnCl_2$ necessary) and the relatiye yields of dihalide are in the same order. R. S. C.

Synthesis of coumarone-1 : 2-dicarboxylic acids. C. F. Koelsch and A. G. Whitney (*J. Amer. Chem. Soc.*, 1941, **63**, 1762).—Crude OPh·C(CO_2Et):C(OH)·CO_2Et (prep. from $Et_2C_2O_4$, NaOEt–EtOH–Et_2O, and OPh·$CH_2{\cdot}CO_2Et$) in H_2SO_4–AcOH gives, according to the temp. and proportions of the acids, 2-*carbethoxybenzfuran*-1-*carboxylic acid* (15—52%), m.p. 186—187°, or the (?) Et_2 ester or, after hydrolysis, the corresponding dicarboxylic acid, m.p. 249—250° (lit. 259—260°). *p*-$C_6H_4Me{\cdot}O{\cdot}C(CO_2Et)$:C(OEt)·$CO_2Et$ (similarly prepared) gives similarly 2-*carbethoxy*-4-*methylbenzfuran*-1-*carboxylic acid*, m.p. 147—148° (*Me*$_3$ ester, m.p. 62·5—63·5°), or the 1 : 2-*dicarboxylic acid*, m.p. 282° (block). OPh·C(CO_2Et):CH·OH gives 27% of coumarilic acid. R. S. C.

Grignard reaction involving the furan nucleus. R. C. Fuson, E. W. Kaiser, and S. B. Speck (*J. Org. Chem.*, 1941, **6**, 845—851).—MgPhBr undergoes exclusively 1 : 2 addition with Ph 2-benzfuryl ketone (I) but 1 : 4-addition with *mesityl* (II) and 2 : 4 : 6-$C_6H_2Pr^{\beta}_3$ (III) 2-*benzfuryl ketones*. Gradual addition of MgPhBr to a boiling solution of (I) in Et_2O affords *diphenyl*-2-*benzfurylcarbinol*, m.p. 133—134°, which does not give a semicarbazone, oxime, acetate, or benzoate. It is oxidised ($Na_2Cr_2O_7$ in AcOH) to $COPh_2$ in 83% yield. (II), m.p. 74·5—76·5°, is obtained from coumarilyl chloride (IV), 1 : 3 : 5-$C_6H_3Me_3$, and $AlCl_3$ in CS_2 at 0° or, with an unidentified *compound*, $C_{18}H_{18}O_4$, m.p. 172—173°, from *o*-OH·C_6H_4·CHO, 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CO{\cdot}CH_2Cl$, and KOH in boiling 95% EtOH. It is converted by MgPhBr, prepared under N_2, into 2-*mesitoyl*-3-*phenyl*-2 : 3-*dihydrobenzfuran* (V), m.p. (indef.) 148—154°; if an inert atm. is not used the cleavage products of (V) (mesitoic acid, m.p. 150—152°, and 3-phenyl*iso*coumaranone, m.p. 114—115°) are obtained. (IV), $AlCl_3$, and 1 : 3 : 5-$C_6H_2Pr^{\beta}_3$ in CS_2 at 0° and subsequently at room temp. afford (III), two forms, m.p. 117—118° and 103—105°, respectively, transformed by MgPhBr under N_2 into 2-2′ : 4′ : 6′-*triisopropylbenzoyl*-3-*phenyl*-2 : 3-*dihydrobenzfuran*, m.p. 140—141°; if air is not rigidly excluded the sole identifiable product is a small amount of 2 : 4 : 6 : 1-$C_6H_2Pr^{\beta}_2{\cdot}CO_2H$. Gradual addition of CHBzBr·CO_2Et to NaOPh in abs. EtOH followed by treatment with conc. H_2SO_4 and alkaline hydrolysis leads to 3-*phenylcoumarilic acid* (V), m.p. 232—233° (decomp.). It is hydrogenated (Raney Ni) at 75°/340 atm. to the H_8-*derivative*, m.p. 160—162°. Addition of Na–Hg to an aq. suspension of (V) affords 3-*phenyl*-2 : 3-*dihydrocoumarilic acid*, m.p. 146—147°, also obtained by adding C_6H_6 to coumarilic acid in presence of $AlCl_3$. When reduction is effected at room temp. the product is an isomeric *acid*, m.p. 186—188°; when heated slowly this acid melts partly, resolidifies, and melts to a clear liquid at 195—196°. H. W.

Interrelation of α-tocopherol and α-tocopherylquinone. M. Tishler and N. L. Wendler (*J. Amer. Chem. Soc.*, 1941, **63**, 1532—1536).—α-Tocopherylquinone (I), prepared by oxidation of α-tocopherol (II) by $AuCl_3$, is best isolated by reduction by $Na_2S_2O_4$-aq. MeOH to the quinol (insol. in light petroleum) and re-oxidation thereof by Ag_2O–$MgSO_4$–Et_2O to (I). Reduction and cyclisation of (I) by conc. HCl–$SnCl_2$–dioxan gives pure (II). The absorption spectrum of (I) has a bicuspid peak at 263—269 mμ. ($E_{mol.}$ 18·7 × 10³). Zn dust–Ac_2O–C_5H_5N at 0° reduces (I) to the *quinol diacetate* (III), m.p. 65°, but Zn dust–Ac_2O–NaOAc gives the triacetate, m.p. 74—75°, also obtained from (III) by Ac_2O–NaOAc. The OH in the side-chain is *tert.* since AcCl gives the *chloride* (IV), m.p. 76—77°, and AcBr the *bromide* (V), m.p. 75—76°. Synthetic (I) yields (V), $[\alpha]_D^{25}$ −2·5° in CCl_4, but (V) obtained from natural (I) has α 0. 2 : 5 : 6-Trimethyl-3-phytylquinol diacetate with HCl–AcOH gives (IV), but with HBr gives (V) and a small amount of a substance, m.p. 65—66°, possibly the impure isomeride formed by alternative addition of HBr. R. S. C.

Reduction of $CCl_3{\cdot}CH(OH)$· group attached to a benzo-α-pyrone nucleus. D. R. Kulkarni and N. M. Shah (*Proc. Indian Acad. Sci.*, 1941, **14**, **A**, 151—157).—Reduction of $CCl_3{\cdot}CH(OH)$· attached to the pyrone ring by Zn and AcOH leads to CHCl:CH· in the case of hydroxycoumarins [those obtained from *m*-$C_6H_4(OH)_2$ or 1 : 2 : 3-$C_6H_3(OH)_3$] but to $CHCl_2{\cdot}CH_2$· when reduction is effected in conjunction with conc. HCl, phenolic OH is absent (as in coumarins obtained from α-$C_{10}H_7{\cdot}OH$ or *p*-cresol), or phenolic OH is protected by acetylation. Reduction of 7-hydroxy-4-methyl-3-βββ-trichloro-α-hydroxyethylcoumarin leads to either 7-hydroxy-4-methyl-3-β-chlorovinylcoumarin, m.p. 254—255° (decomp.), or -3-ββ-*dichloroethylcoumarin* (I), m.p. 206—207° [*acetate*, m.p. 101—102°, also obtained by reducing (Zn and AcOH) 7-acetoxy-4-methyl-3-βββ-trichloro-α-acetoxyethylcoumarin, and de-acetylated to (I)]. The following are analogously obtained : 7 : 8-dihydroxy-4-methyl-3-β-chlorovinylcoumarin, m.p. 231—232°, and -3-ββ-*dichloroethylcoumarin*, m.p. 195—196° (*acetate*, m.p. 163—164°); 5-*hydroxy*-4 : 7-*dimethyl*-3-β-*chlorovinylcoumarin*, m.p. 251—252° (*acetate*, m.p. 148—149°), and -3-ββ-*dichloroethylcoumarin*, m.p. 242° (*acetate*, m.p. 157°); 5 : 7-*diacetoxy*-4-*methyl*-3-ββ-*dichloroethylcoumarin*, m.p. 121—122°, deacetylated to the 5 : 7-$(OH)_2$-*compound*, m.p. 246—247°; 4′-*methyl*-3-ββ-*dichloroethyl*-1 : 2-α-*naphthapyrone*, m.p. 221—222°; 4 : 6-*dimethyl*-3-ββ-*dichloroethylcoumarin*, m.p. 206—207°. H. W.

Heterocyclic compounds. XIV. Coumarins from 2-acetyl-4-ethylresorcinol and β-ketonic esters. R. D. Desai and C. K.

Mavani (*Proc. Indian Acad. Sci.*, 1941, **14, A**, 100—104).—2 : 4 : 1 : 3-$C_6H_3AcEt(OH)_2$ (I) condenses much more readily than resacetophenone with substituted $CH_2Ac{\cdot}CO_2Et$ and similar compounds showing that the Pechmann reaction is not hindered by negative groups at $C_{(4)}$ in the *m*-$C_6H_4(OH)_2$ mol. The constitution of each coumarin is established by its rational synthesis from 4 : 1 : 3-$C_6H_3Et(OH)_2$, acetylating the resulting coumarin, and subjecting it to the Fries migration. $CHMeAc{\cdot}CO_2Et$ and (I) in 73% H_2SO_4 at room temp. for 36 hr. give 7-*hydroxy*-8-*acetyl*-3 : 4-*dimethyl*-6-*ethylcoumarin* (II), m.p. 121° (yield 75%). 4 : 1 : 3-$C_6H_3Et(OH)_2$ and $CHMeAc{\cdot}CO_2Et$ similarly afford 7-*hydroxy*-3 : 4-*dimethyl*-6-*ethylcoumarin*, m.p. 240°, the *acetate*, m.p. 150°, of which is isomerised by $AlCl_3$ at 140° to (II). The following are obtained analogously: 7-*hydroxy*-8-*acetyl*-, m.p. 147°, and 7-*hydroxy*-, m.p. 216°, -4-*methyl*-3 : 6-*diethylcoumarin* (*acetate*, m.p. 131°); 7-*hydroxy*-8-*acetyl*-, m.p. 129°, and 7-*hydroxy*-, m.p. 189°, -4-*methyl*-6-*ethyl*-3-*propylcoumarin* (*acetate*, m.p. 133°); 7-*hydroxy*-8-*acetyl*-, m.p. 124°, and 7-*hydroxy*-, m.p. 159°, -4-*methyl*-6-*ethyl*-3-*butylcoumarin*, m.p. 159° (*acetate*, m.p. 114°); 7-*hydroxy*-8-*acetyl*-, m.p. 106°, and 7-*hydroxy*-, m.p. 202°, -4-*methyl*-6-*ethyl*-3-*allylcoumarin*, m.p. 202° (*acetate*, m.p. 123°); 7-*hydroxy*-8-*acetyl*-, m.p. 154°, and 7-*hydroxy*-, m.p. 232°, -4-*phenyl*-6-*ethylcoumarin* (*acetate*, m.p. 151°).

H. W.

Nuclear methylation of β-resorcylaldehyde.—See A., 1942, II, 98.

Benzopyrylium salts. III. Syntheses from substituted coumarins and chromones. R. L. Shriner and R. B. Moffett (*J. Amer. Chem. Soc.*, 1941, **63**, 1694—1698; cf. A., 1941, II, 51).—2 : 3-Diphenyl-6-methylchromone and, best (73%), an excess of *p*-$C_6H_4Me{\cdot}MgBr$ in Et_2O–C_6H_6 at room temp. give 2 : 3-*diphenyl*-4-p-*tolyl*-6-*methyl*-1 : 4-*benzpyran*-4-*ol* (I), m.p. 142—144°. *p*-Tolyl *p*-toluate and $AlCl_3$ in boiling CS_2 give 82% of 2-*hydroxy*-5 : 4′-*dimethylbenzophenone* (II), m.p. 89·5—90°, which with $CH_2Ph{\cdot}CO_2Na$ and $CH_2Ph{\cdot}COCl$ at 180—190° and later 190—200° gives 33·8% of 3-*phenyl*-4-p-*tolyl*-6-*methylcoumarin*, m.p. 183·5—184·5°, converted by MgPhBr in Et_2O–C_6H_6 into 2 : 3-*diphenyl*-4-p-*tolyl*-6-*methyl*-1 : 2-*benzpyran*-2-*ol* (III), m.p. 142—144° (decomp.), and, if an excess of MgPhBr is used, αβ-*diphenyl*-β-p-*tolyl*-β-2-*hydroxy*-5-*methylphenylpropiophenone*, m.p. 141·5—143° (converted at 140—150° into 2 : 3 : 4-*triphenyl*-4-p-*tolyl*-6-*methyl*-1 : 4-*benzpyran*, m.p. 185—188°). (I) or (III) gives 3-*phenyl*-4-p-*tolyl*-6-*methylflavylium ferrichloride*, m.p. 183·5—184·5°, and *perchlorate*, m.p. 235·5—238·5° (decomp.), and with HCl–MeOH gives 2-*methoxy*-2 : 3-*diphenyl*-4-p-*tolyl*-6-*methyl*-1 : 2-*benzpyran*, m.p. 127—128° (126—127°), converted by HCl–Et_2O into 3-*phenyl*-4-p-*tolyl*-6-*methylflavylium chloride hydrochloride*, m.p. 183—191° (decomp.), and by O_3 in CCl_4 into (II). These results favour the view that flavylium salts contain a mobile allylic system.

R. S. C.

New preparation of compounds resembling tocopherol. P. Karrer and W. Fatzer (*Helv. Chim. Acta*, 1941, **24**, 1317—1321).—Prolonged passage of dry HCl through a mixture of 2 : 5 : 4 : 6 : 1-$(OH)_3C_6HMe_2{\cdot}CHO$, COPhMe, and anhyd. HCO_2H gives 6-*hydroxy*-2-*phenyl*-5 : 7-*dimethylbenzopyrylium chloride*, m.p. ~130° (decomp.) (corresponding *picrate*), which contains H_2O of crystallisation which cannot be removed without partial decomp. It is readily reduced (H_2–PtO_2 in AcOH) to 6-*hydroxy*-2-*phenyl*-5 : 7-*dimethylchroman* (I), m.p. 125°, which resembles closely the tocopherols. Like these, it reduces warm $AgNO_3$ and is quantitatively oxidised by $AuCl_3$ to non-cryst. 2 : 4-*dimethyl*-1-γ-*hydroxy*-γ-*phenylpropyl*-p-*benzoquinone*. (I) can be determined colorimetrically with $FeCl_3$ and dipyridyl (II) since it reduces 2 equivs. of $FeCl_3$ to $FeCl_2$, which gives a red, complex salt with (II). The absorption curve of (I) is closely similar to that of the tocopherols. 6-*Hydroxy*-2′-p-*hydroxyphenyl*-5 : 7-*dimethylbenzopyrylium chloride*, decomp. 233—235°, obtained similarly from *p*-$C_6H_4Ac{\cdot}OH$, is readily reduced to 6-*hydroxy*-2-p-*hydroxyphenyl*-5 : 7-*dimethylchroman* (III), m.p. 228°, which reduces warm $AgNO_3$ and $AuCl_3$ at room temp. In the respective doses of 50—100 mg. and 30—60 mg. (I) and (III) are completely inactive pharmacologically.

H. W.

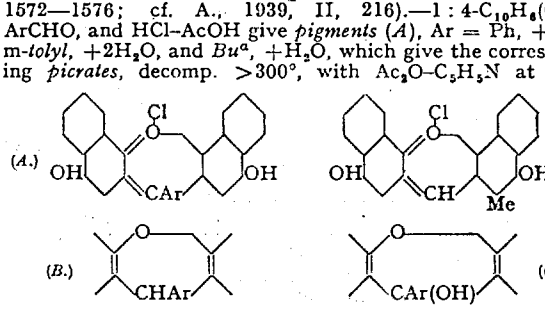
Colouring matter of the flowers of *Hibiscus cannabinus*; constitution of cannabiscetin. K. Neelakantam, P. S. Rao, and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, **14, A**, 105—111).—The methylated spirit extract of the dried petals deposits *cannabiscitrin* (I) and the mother-liquor when diluted with H_2O yields *cannabiscetin* (II). The $Pb(OAc)_4$ fraction consists mainly of (I), which is difficult to purify but readily gives (II) after hydrolysis. The basic acetate fraction is very small so that the colouring matter is mainly (I) with small quantities of (II). (I), decomp. ~245°, is $C_{21}H_{20}O_{16}$. With alkaline buffer solutions it yields two characteristic colours, green and orange, the primary yellow being very fugitive. It gives a colourless *nona-acetate* which melts to a glassy mass at 200—202° but does not flow at 260°. (I) is hydrolysed by dil. H_2SO_4 to (II) and glucose. (II), m.p. >350°, is $C_{15}H_{10}O_6$. It gives a brown-black colour with $FeCl_3$ and a sequence of colours with dil. alkali. With alkaline buffer solutions the characteristic colours are green, blue, crimson, and purple, thus permitting ready discrimination between (I) and (II). It gives a *hexa-acetate*, m.p. 215—217°, and a *Me*$_6$ *ether* (III), m.p. 175—176°. It gives a dark red ppt. with $Pb(OAc)_4$ and is oxidised by air in alkaline solution to gallic acid. With *p*-$O{:}C_6H_4{:}O$ it yields the "gossypetone" reaction. (III) and boiling 53% KOH afford 3 : 4 : 5 : 1-$C_6H_2(OMe)_3{\cdot}CO_2H$. Hence (II) is 3 : 5 : 8 : 3′ : 4′ : 5′-*hexahydroxyflavone*.

H. W.

Constitutional features of anthoxanthins in relation to the morin reaction in analytical chemistry. I. Naturally occurring hydroxyflavonols and flavanones. K. Neelakantam and L. R. Row (*Proc. Indian Acad. Sci.*, 1941, **14, A**, 307—312).—Comparison of the behaviour of naringenin (I), kæmpferol (II), herbacetin (III), morin (IV), quercetin (V), gossypetin (VI), quercetagetin (VII), and butin under the conditions of the (IV) reaction shows that (IV) is exceptional in giving a very prominent fluorescence; none of the others gives any fluorescence with Al or Be in daylight and the fluorescence observed under the lamp is not so intense. Since the only constitutional difference between (IV) and (V) is in the 2′ instead of 3′ position of OH in the side C_6H_3 nucleus, the difference in behaviour may be due to the 2′ position of one OH. The intensifying effect of OH at $C_{(2')}$ on the fluorescence given by a compound with OH at $C_{(4)}$ is shown by comparison of (II) and (IV) and is supported by comparison of (V) with (VI). The inhibitory effect of OH at $C_{(6)}$ is established by the behaviour of (VII). The exhibition of fluorescence by (I) and (II) proves that OH at $C_{(3)}$ is not essential for the appearance of fluorescence with metals. It is probable that OH at $C_{(2')}$ alone or in conjunction with OH at $C_{(4)}$ is responsible for the brilliant fluorescence obtained with (IV) and metals. This conclusion appears to be supported by the observation that (IV), unlike other flavonols, yields an anhydrosulphate, $C_{15}H_8O_6{\cdot}H_2SO_4$, with conc. H_2SO_4 and this behaviour is closely related to the presence of OH at $C_{(2')}$.

H. W.

Anthocyanidin-like pigments from α-napthaquinols. (Mrs.) M. Fieser and L. F. Fieser (*J. Amer. Chem. Soc.*, 1941, **63**, 1572—1576; cf. A., 1939, II, 216).—1 : 4-$C_{10}H_6(OH)_2$, ArCHO, and HCl–AcOH give *pigments* (*A*), Ar = Ph, $+H_2O$, m-*tolyl*, $+2H_2O$, and *Bu*$^{\alpha}$, $+H_2O$, which give the corresponding *picrates*, decomp. >300°, with Ac_2O–C_5H_5N at room



temp. give *diacetates*, (*a*) darken at 240°, decomp. 265—270° (lit. decomp. 246°), (*b*) —, and (*c*) darken at ~240°, decomp. 265—275°, respectively, and with Zn dust–Ac_2O give the *leuco-base diacetates* (*B*), (*a*) darken at 230°, decomp. ~260—270°, (*b*) —, and (*c*) decomp. 275—280°, respectively. The ψ-bases are (*C*). *Pigments*, as (*D*), m.p. >250°, are formed from 2-methyl- or 2 : 6-dimethyl-1 : 4-naphthaquinol with HCl–AcOH, best (40—44%) if 1 mol. of the corresponding quinone is also present.

R. S. C.

Cannabis indica. **VIII. Further analogues of tetrahydrocannabinol.** P. B. Russell, A. R. Todd, S. Wilkinson, A. D. Macdonald, and G. Woolfe (*J.C.S.*, 1941, 826—829; cf. A., 1941, II, 173).—The following are described: 5-*hydroxy*-5′-*methyl*-7-*ethyl*-, m.p. 204—205°, -*n*-propyl-, m.p. 92—93° (lit.

145—146°), -*n*-butyl-, -*n*-hexyl-, -*n*-heptyl-, -iso*amyl*-, m.p. 200—201° (*acetate*, m.p. 98—99°), and -iso*hexyl*-3 : 4-cyclo*hexenocoumarin*, m.p. 177—180°; 6″-*hydroxy*-2 : 2 : 5′-*trimethyl*-4″-*ethyl*-, m.p. 100—101°, -4″-iso*amyl*-, m.p. 56—57°, and -4″-iso*hexyl*-, b.p. 203°/1 mm., and 6″-*hydroxy*-5′ : 4″-*dimethyl*-2 : 2-*di*-n-*propyl*-, b.p. 165°/0·1 mm., and -*di*-n-*butyl*-, b.p. 170—175°/0·1 mm., and 4″ : 6″-*dihydroxy*-2 : 2 : 5′-*trimethyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzopyran*, b.p. 200°/0·1 mm.; and 5-*hydroxy*-2 : 2 : 4 : 7-*tetramethyl*-3-n-*butyl*-Δ^3-*chromen*, b.p. 160—170°/0·1 mm. The hashish activity of these substances is discussed (cf. Adams *et al.*, A., 1941, II, 341). F. R. S.

Compounds of the cannabinol type. I. Synthesis of some compounds related to tetrahydrocannabinol. T. H. Bembry and G. Powell (*J. Amer. Chem. Soc.*, 1941, **63**, 2766—2768).—Interaction of tetrahydrobenzcoumarins (cf. Sen *et al.*, A., 1928, 1254) with MgRBr in Et_2O–C_6H_6 gives 2 : 2 : 5″-*trimethyl*- (**I**), m.p. 72—73°, 6″-hydroxy-2 : 2-dimethyl-4″-*n*-amyl- (**II**), b.p. 175—176°/0·5 mm. (Adams *et al.*, A., 1941, II, 331), 6″-*hydroxy*-4″-*methyl*-2 : 2-*di*-*ethyl*-, b.p. 160—162°/0·5 mm., -n-*propyl*-, b.p. 164—165°/0·5 mm., and -*n*-amyl-, b.p. 183—185°/0·5 mm., 6″-hydroxy-5′-methyl-2 : 2-diethyl-*n*-amyl-, b.p. 178—179°/0·5 mm. (*loc. cit.*), -2 : 2-di-*n*-propyl-4″-*n*-amyl-, b.p. 190—192°/0·5 mm. (*loc. cit.*), and -2 : 2-di-*n*-butyl-4″-*n*-amyl-, b.p. 198—200°/0·5 mm. (*loc. cit.*), -3′ : 4′ : 5′ : 6′-tetrahydrobenzpyran. With Me_2SO_4–NaOH–MeOH–H_2O 3′ : 4′ : 5′ : 6′-tetrahydrocannabinol (**III**) gives the 6″-*Me*, b.p. 200—210°/15 mm., and with $C_5H_{11}Br$–NaOEt–EtOH gives the 6″-*amyl ether*, b.p. 244°/13 mm. With 3 : 5 : 1-$(NO_2)_3C_6H_3$·CON_3–C_6H_6 and then abs. EtOH, (**II**) and (**III**) give the 3 : 5-*dinitrophenylurethanes*, m.p. 210—212° (gas; corr.) and 191—192° (decomp.), respectively. S at 200—240° dehydrogenates (**I**) to 2 : 2 : 5″-trimethyldibenzpyran, m.p. 58° (Cahn, A., 1932, 1302). R. S. C.

Photochemical decomposition of rotenone.—See A., 1942, I, 109.

M.p. of toxicarol and of related compounds. S. H. Harper (*J.C.S.*, 1941, 878).—The m.p. of *dl*-toxicarol, sumatrol, *dl*-deguelin, rotenone, elliptone, and related compounds are higher in Pyrex glass than in soft glass. No difference was observed in the m.p. of *l*-α-toxicarol. F. R. S.

Depression of the m.p. of α-toxicarol and related compounds in soft-glass capillary tubes. H. A. Jones and J. W. Wood (*J. Amer. Chem. Soc.*, 1941, **63**, 1760—1761).—The m.p. of α- (**I**) (230—231°, 205—206°) and β-toxicarol [sample (*a*) 180—182°, 176—178°, and (*b*) 165—167°, 164·5—165·5°, partial melting, complete at 191°], rotenone (**II**) (163—164°, 159·5—160·5°), and deguelin (169—170°, 163·5—164·5°), but not anthracene, depend on the alkalinity of the glass. Figures in parentheses are for Pyrex and soft glass respectively. In very alkaline glass (**I**) and (**II**) have m.p. 200—201° and 155—156° respectively. R. S. C.

Effect of soft glass on m.p. of rotenone. H. A. Jones [*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 819).—The m.p. of rotenone (pure) was 163—164° in Pyrex, 159·5—160·5° in soft glass, and 155—156° in Corning electrode glass. With impure samples (m.p. 161—162°, and 151—153·5° in Pyrex), the depressions of m.p. were smaller. J. D. R.

Nitro- and amino-acetals derived from polyhydric nitro-alcohols. M. Senkus (*J. Amer. Chem. Soc.*, 1941, **63**, 2635—2636).—Distillation of H_2O from NO_2·$CMe(CH_2$·$OH)_2$ (**I**) or NO_2·$CEt(CH_2$·$OH)_2$ (**II**) (1) with 36% CH_2O (1 mol.) and a little *p*-C_6H_4Me·SO_3H gives 5-*nitro*-5-*methyl*-, m.p. 71·0°, and -5-*ethyl*-1 : 3-*dioxan*, m.p. 53·2°. Removal by distillation of all H_2O from (**I**), (**II**), or NO_2·$C(CH_2$·$OH)_3$ with RCHO and a little *p*-C_6H_4Me·SO_3H in C_6H_6 gives 5-*nitro*-5-*methyl*-2-n-*propyl*-, m.p. 47·8°, 5-*nitro*-5-*methyl*-2-α-*ethyl*-n-*amyl*-, b.p. 154—155·5°/5 mm., 5-*nitro*-2-*phenyl*-5-*methyl*-, m.p. 118·3°, 5-*nitro*-5-*ethyl*-2-α-*ethyl*-n-*amyl*-, b.p. 163—164·5°/5 mm., 5-*nitro*-5-*ethyl*-n-*undecyl*-, m.p. 42·5°, 5-*nitro*-5-*hydroxymethyl*-2-n-*propyl*-, m.p. 69·8°, -2-α-*ethyl*-n-*propyl*-, m.p. 70·5°, -2-n-*hexyl*-, m.p. 59·8°, -2-α-*ethyl*-n-*amyl*-, b.p. 183—184·5°/5 mm., and -2-n-*undecyl*-, m.p. 67·9°, -1 : 3-*dioxan*. Reduction by H_2–Raney Ni in MeOH at 60—75°/1000—1500 lb. gives 5-*amino*-5-*methyl*-, b.p. 86°/50 mm., and -5-*ethyl*-, b.p. 186° [N-*CH*$_2$·, m.p. 91·6°, and β-*ethyl*-n-*hexylidene*, b.p. 139·5—141·2°/10 mm., hydrogenated (Raney Ni) to N-*Me*, b.p. 192°, and N-β-*ethyl*-n-*hexyl* derivatives, b.p. 146—147°/10 mm.], 5-*amino*-5-*methyl*-2-n-*propyl*-, b.p. 197·3°/748 mm. (N-*CHPh*·, m.p. 33·0°, and N-CH_2Ph derivative, b.p. 172·5—173°/10 mm.), 5-*amino*-5-*methyl*-2-α-*ethyl*-n-*amyl*-, b.p. 123·0—124·4°/10 mm., 5-*amino*-2-*phenyl*-5-*methyl*-, m.p. 84°, 5-*amino*-5-*ethyl*-2-α-*ethyl*-n-*amyl*-, b.p. 137·2—137·8°/10 mm., 5-*amino*-5-*ethyl*-2-n-*undecyl*-, b.p. 198—201·5°/10 mm., 5-*amino*-5-*hydroxymethyl*-2-n-*propyl*-, m.p. 62°, -2-α-*ethyl*-n-*propyl*-, m.p. 43°, -n-*hexyl*-, m.p. 83·6°, and -n-*undecyl*-, m.p. 103·9°, -1 : 3-*dioxan*. The NO_2-dioxans are stable to dil. alkali and boiling H_2O, slowly decompose at 150°, and are hydrolysed by hot mineral acid (as also are the NH_2-compounds). *n* and *d* are recorded for the liquid products. R. S. C.

Action of formaldehyde on *o*-chlorophenol and 2 : 4-dichlorophenol. C. A. Buehler, R. L. Brown, J. M. Holbert, J. G. Fulmer, and G. W. Parker (*J. Org. Chem.*, 1941, **6**, 902—907).—*o*-C_6H_4Cl·OH, 40% CH_2O, and conc. HCl at room temp. and then at 45—50° yield 3-*chloro*-4-*hydroxybenzyl chloride*, m.p. 92—93°, converted by H_2O containing $AgNO_3$ at 70° into 3-*chloro*-4-*hydroxybenzyl alcohol* (**I**), m.p. 127°, obtained synthetically by chlorination of *p*-OH·C_6H_4·CHO to 4 : 3 : 1-OH·C_6H_3Cl·CHO, which is reduced (Raney Ni in EtOAc). *o*-C_6H_4Cl·OH, 40% CH_2O, and 60% H_2SO_4 at 60—65° afford 3 : 3′-dichloro-4 : 4′-dihydroxydiphenylmethane (**II**), m.p. 103—104° (*diacetate*, m.p. 126·5—127·5°; *dibenzoate*, m.p. 116—116·5°), transformed by Cl_2 in glacial AcOH at room temp. into the 3 : 3′ : 5 : 5′-Cl_4-compound, m.p. 184—185°. (**II**) is obtained synthetically by treating a solution of (**I**) in *o*-C_6H_4Cl·OH with HCl. Passage of HCl through a mixture of 2 : 4 : 1-$C_6H_3Cl_2$·OH (**III**), 40% CH_2O, H_2SO_4, and conc. HCl at 35—40° leads to 6 : 8-*dichlorobenzdehydro*-1 : 3-*dioxan*, m.p. 109—109·5°, oxidised to 6 : 8-*dichlorobenzdehydro*-1 : 3-*dioxan*-4-*one*, m.p. 114°. This is converted by boiling dil. NaOH into 3 : 5-dichlorosalicylic acid, m.p. 220° (Me ester, m.p. 148—149°). Under somewhat different conditions (**III**) is transformed into 3 : 5-*dichloro*-2-*hydroxybenzyl chloride*, m.p. 82—84°, converted by H_2O at 50° into the alcohol, m.p. 80—81°. 6 : 8-*Dichloro*-2-*phenylbenzdehydro*-1 : 3-*dioxan* has m.p. 83·5—85·0°. H. W.

Synthesis of 2″ : 3″-7 : 8-furanoflavone. B. L. Manjunath and A. Seetharamiah (*J. Mysore Univ.*, 1940, **B**, 13—16).—3-Hydroxybenzfuran-4-carboxylic acid (furanosalicylic acid) (cf. A., 1939, II, 122) and CH_2N_2 give the *Me* ester, m.p. 109°, further methylated through the Na salt and MeI–MeOH (reflux) to the O-*Me ether*, b.p. 114—116°/0·3 mm., hydrolysed by 10% KOH–EtOH to 3-*methoxybenzfuran*-4-*carboxylic acid*, m.p. 149°. The corresponding acid *chloride*, m.p. 71—72°, and Zn–MeI in PhMe at room temp. afford 3-*methoxy*-4-*acetylbenzfuran*, m.p. 56—57° (purified through the *semicarbazone*, m.p. 165°), converted by HI (*d* 1·7)–AcOH at 100° (bath) into 3-*hydroxy*-4-*acetylbenzfuran*, m.p. 92°, and thence by Bz_2O–NaOBz at 180—185° into 2″ : 3″-7 : 8-*furanoflavone*, m.p. 229°. A. T. P.

Chemotherapeutic studies in the thiophen series. I. Synthesis of 2-sulphanilamidothiophen. C. von Seemann and C. C. Lucas (*Canad. J. Res.*, 1941, **19**, **B**, 291—295).—2-Aminothiophen (prep. described) and *p*-NHAc·C_6H_4·SO_2Cl [C_5H_5N gives a (?) C_5H_5N salt, m.p. 114° (previous sintering)] in aq. $COMe_2$–Et_2O (in H_2; apparatus described) affords 2-*N*^{4}-acetylsulphanilamido-, m.p. 195°, and thence [aq. NaOH at 100° (bath)] 2-sulphanilamido-thiophen, m.p. 155° (cf. Bost *et al.*, A., 1941, II, 332). A. T. P.

Isologues of 9 : 10-dimethyl-1 : 2-benzanthracene containing sulphur and selenium. E. B. Hershberg and L. F. Fieser (*J. Amer. Chem. Soc.*, 1941, **63**, 2561—2564).—2-Methylanthraquinone and Cl_2 in 3% oleum at 3—5° give the 1-Cl-derivative, new m.p. 172·3—172·8°, converted by Br in $PhNO_2$ at 170—175° into 1-chloro-2-dibromomethylanthraquinone, which in conc. H_2SO_4 (N_2) at 120° (less well, with $FeCl_3$–AcOH) gives the 2-aldehyde, new m.p. 199·6—200·1°. With $CH_2(CO_2H)_2$–C_5H_5N at 100°, less well with Ac_2O–NaOAc, this gives β-1-*chloro*-2-*anthraquinonylacrylic acid* (**I**) (68%), m.p. 286·5—287·5° (decomp.), which with aq. Na_2S_x at 130° gives *thiopheno*-2′ : 3′-1 : 2-*anthraquinone*-5′-*carboxylic acid* (63%), softens at 345—350°, m.p. 361—363° (decomp.; block), converted in presence of basic Cu carbonate in quinoline at 230—240° into *thiopheno*-2′ : 3′-1 : 2-*anthraquinone* (84%), m.p. 219·6—220·1°. Heating with MgMeCl in Et_2O–C_6H_6 at 70—80° and then with HI–AcOH and reduction of the resulting CH_2I compound by $SnCl_2$–conc. HCl–dioxan gives 9 : 10-*dimethylthiopheno*-2′ : 3′-1 : 2-*anthraquinone* (37%), m.p. 123·6—124·2° [*semipicrate*, m.p. 125·5—126°; *s*-$C_6H_2(NO_2)_3$

compound, m.p. 172·5—173°]. Na_2Sc_x–EtOH–H_2O and (**I**) at 100—110° give *selenopheno-2′ : 3′-1 : 2-anthraquinone-5′-carboxylic acid* (77%), m.p. 347—349° (decomp.), and thence, as above, *selenopheno-2′ : 3′-1 : 2-anthraquinone*, m.p. 213·5—214·5°, and its 9 : 10-Me_2 derivative, m.p. 118—118·5° [*picrate*, m.p. 145·5—146°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 173·5—174°]. 4 : 9-Dimethyl-5 : 6-benzthiophanthrene (Sandin *et al.*, A., 1941, II, 218) is highly carcinogenic. R. S. C.

β-Piperidino-α-di-*n*-alkylaminopropiophenone dihydrobromides. H. L. Davis (*J. Amer. Chem. Soc.*, 1941, **63**, 1677—1679).—COPh·CHBr·CH_2Br (prep. from CH_2Br·CHBr·CH_2·OH etc. modified) and NHR_2 (2 mols.) in Et_2O at 20—25° give *β-bromo-α-di-methyl-* (**I**), m.p. 165—166°, *-ethyl-* (**II**), m.p. 161—162°, *-n-propyl-* (**III**), m.p. 140—141°, *-n-butyl-*, m.p. 128—129°, and *-n-amyl-*, m.p. 127·5—129°, *-aminopropiophenone hydrobromide*. With NHPh·NH_2–EtOH or *p*-C_6H_4Br·NH_2,HCl–NaOAc–H_2O–EtOH, (**I**) gives 1 : 3-diphenyl- (**IV**) (35·13%) and *3-phenyl-1-p-bromophenyl-pyrazole*, m.p. 137—138°, respectively. NHPh·NH_2 and (**II**) in EtOH give (**IV**) (11·28%) and a *substance*, m.p. 152—153°. With piperidine–Et_2O and later HBr–EtOH at 15—20°, (**I**), (**II**), and (**III**) give *β-piperidino-α-di-methyl-*, m.p. 190—191°, *-ethyl-*, m.p. 164—165°, and *-n-propyl-aminopropiophenone dihydrobromide*, m.p. 154—155°, respectively, which have no vasopressor or local anæsthetic activity. R. S. C.

Alkali and alkaline-earth metals as catalysts in the hydrogenation of organic compounds.—See A., 1942, I, 107.

β-2- and -4-Pyridylalkylamines. L. A. Walter, W. H. Hunt, and R. J. Fosbinder (*J. Amer. Chem. Soc.*, 1941, **63**, 2771—2773).—*β-2-Pyridylethyl-methyl-*, m.p. 148—149°, and *-diethyl-amine dihydrochloride*, m.p. 171—172°, are described. Addition of, successively, PhBr, 2-methylpyridine, and MeCHO to Li in Et_2O–N_2 gives 4—6% of *β-2-pyridyliso*propyl alcohol, b.p. 110—111°/10 mm.; the derived bromide with NH_2Me–EtOH (excess) at 100° gives *β-2-pyridyliso*propylmethylamine, hygroscopic, b.p. 72°/2 mm. (*dihydrochloride*, m.p. 158—158·5°). *β*-2-Pyridylpropionitrile (prep. from the bromide by NaCN in boiling 80% EtOH), b.p. 85—87°/1 mm., with H_2O_2–aq. KOH at 40° gives *β-2-pyridylpropionamide* (**I**), m.p. 129—130° or 76—77°. Reduction of *β*-2-pyridylacrylic acid by H_2–Raney Ni in aq. alkali at 40 lb. and subsequent esterification gives Me *β*-2-pyridylpropionate, b.p. 102—103°/2 mm., converted by aq. NH_3 at 0° into (**I**). (**I**) added to NaOMe–MeOH, treated with Br at 0°, and then boiled gives *Me N-β-phenylethylurethane* (**II**), m.p. 53—54°, hydrolysed by HCl to *β*-2-pyridylethylamine (**III**) (*dihydrochloride*, m.p. 185—186°). The *methiodide*, m.p. 110—111°, of (**II**) with AgCl–H_2O and then boiling HCl gives the *methochloride hydrochloride*, m.p. 191—193°, of (**III**). *β*-4-Pyridylacrylic acid [prepared from αaa-trichloro-γ-4-pyridyl-*β*-propanol (improved prep.)] gives *β*-4-pyridylpropionic acid (Me ester, b.p. 95°/2 mm.; *amide*, m.p. 166—167°) and thence, as above, Me *N-β*-4-pyridylethylurethane (*hydrochloride*, m.p. 132—133°; *methiodide*, m.p. 121—122°) and *β*-4-pyridylethylamine (*dihydrochloride*, m.p. 222°; *methochloride hydrochloride*, m.p. 186—187°). Pharmacological properties of the amines are briefly recorded and discussed. R. S. C.

Substituted 3-diazoacetylpyridines and their transformation products. Preparation of β-homoquinolinic and β-homonicotinic acid. K. Miescher and H. Käg (*Helv. Chim. Acta*, 1941, **6**, 1471—1479).—Gradual addition of 2-aminonicotinic acid to PCl_5 in AcCl at room temp. gives 2-aminonicotinyl chloride hydrochloride (**I**), from which aq. K_2CO_3–Et_2O liberates *2-aminonicotinyl chloride*, decomp. ~110°. Gradual addition of (**I**) to CH_2N_2 in CH_2Cl_2 at −10° and then at room temp. leads to *2-amino-3-diazoacetylpyridine* (**II**), decomp. 163°. (**II**) does not undergo the customary Arndt–Eistert reaction; with alkalis (NaOH) or with NH_3 it evolves N_2 but gives only black solutions whereas N_2 is not evolved when it is boiled with alcohols and Ag_2O. It shows normal behaviour towards acids. With H_2SO_4 it loses N_2 and yields 2-amino-3-sulphoxyacetylpyridine, 2 : 3-NH_2·C_5H_3N·CO·CH_2·O·SO_3H, m.p. >350°, accompanied by *2-amino-3-hydroxyacetylpyridine*, m.p. 139·5°. With 5*N*-HCl and HBr (*d* 1·5) (**II**) yields *2-amino-3-chloro-*, m.p. 146° (decomp.), and *2-amino-3-bromo-* (**III**), m.p. 113° (*hydrobromide*, decomp. 217°), *-acetylpyridine*. (**III**) and $(CH_2)_6N_4$ in $CHCl_3$ give an additive *product*, transformed by boiling HBr into *2-amino-3-aminoacetylpyridine dihydrobromide*, decomp. 254°; the corresponding free base is very freely sol. in H_2O and very unstable. Anhyd. HCO_2H and (**II**) readily yield *2-amino-3-formyloxyacetylpyridine*, m.p. 143°. *2-Amino-3-acetoxyacetylpyridine*, m.p. 138—139°, is obtained from (**II**) and AcOH at 100° or from (**III**) and aq. NaOAc. Gradual addition of 2-carbomethoxynicotinyl chloride to CH_2N_2 in CH_2Cl_2 at −10° affords *2-carbomethoxy-3-diazoacetylpyridine*, m.p. 68—70°. This in presence of alkalis or NH_3 gives only black solutions whereas it is smoothly converted by Ag_2O in warm MeOH into Me_2 *β-homoquinolinate*, b.p. 110°/0·05 mm., hydrolysed by alkali to *β-homoquinolinic acid* [*2-carboxy-3-pyridylacetic acid*], m.p. (anhyd.) 182—183° (decomp.), which is decarboxylated at 180°, best in presence of $NPhMe_2$ to *β-homonicotinic acid* [*pyridyl-3-acetic acid*], m.p. 144°. H. W.

2-Sulphamilamidopyridine-N^2-methylenesulphinic acid.—See B., 1942, III, 61.

Further modification of the Skraup synthesis of quinoline. R. F. H. Manske, F. Leger, and G. Gallagher (*Canad. J. Res.* 1941, **19**, **B**, 318—319).—To $FeSO_4$,$7H_2O$ are added NHAcPh, $PhNO_2$, a solution of H_3BO_3 in glycerol, and conc. H_2SO_4, and the mixture is refluxed. The reaction is less violent than when NH_2Ph is used; more quinoline and less tar are produced. Similarly *p*-C_6H_4Ph·NHAc affords a good yield of 6-phenylquinoline (cf. Cohn, A., 1930, 1445). A. T. P.

Use of selenium dioxide in the preparation of quinoline aldehydes. H. Kaplan (*J. Amer. Chem. Soc.*, 1941, **63**, 2654—2655).—4- or 2-Methylquinoline (**I**) with fresh crude or sublimed SeO_2 gives the aldehyde (**II**), but with old SeO_2 (which cannot be activated by sublimation or treatment with HNO_3) gives *αβ-di-4-quinolylethylene*, m.p. 207° [also prepared from (**I**), (**II**), and a little Ac_2O at 110°], or the quinaldoin, COR·CHR·OH, m.p. 269—271° [also obtained from (**II**) by KCN–EtOH–H_2O], respectively. R. S. C.

Organo-metallic derivatives of carbazole and quinoline. Amides of quinoline-3-carboxylic acid. H. Gilman and S. M. Spatz (*J. Amer. Chem. Soc.*, 1941, **63**, 1553—1557).—With $LiBu^a$ in boiling C_6H_6, followed by CO_2–Et_2O, 3-bromocarbazole gives 57·8% of carbazole-3-carboxylic acid, 3-bromo- and -iodo-9-ethylcarbazole give 71·1 and 67%, respectively, of the 3-carboxylic acid, 3 : 6-*di-bromo-* (**I**), m.p. 142—143°, and -iodo-9-ethylcarbazole (**II**), new m.p. 154°, give 84 and 79%, respectively, of 9-ethylcarbazole-3 : 6-dicarboxylic acid. $MgBu^a$Br and (**II**) give only 3·7% of *3-iodo-9-ethylcarbazole-6-carboxylic acid* (**III**), m.p. 280—282°, but (**I**) does not react. 3-Bromoquinoline and $LiBu^a$ in Et_2O at −45° (5 min.) give, after treatment with CO_2, 35—47·5% of quinoline-3-carboxylic acid [Et ester, m.p. 69—69·5° (lit. 66—67°)], but at higher temp. LiR adds to the C:N. Quinoline and $LiBu^a$ at −35° give Li 3-*n*-butyl-3 : 4-dihydro-4-quinolyl and 93·5% of 2-*n*-butylquinoline, but 2-chloroquinoline gives only 1—2% of a *Cl-acid*. 3-Iodo-1-methylquinoline with $LiBu^a$–Et_2O, best (53%) at −5°, and later CO_2 gives 1-methylquinoline-3-carboxylic acid, m.p. 153—154° [Cu salt; oxalate, new m.p. 178·5° (decomp.) (variable)]. 97% of (**I**) is obtained from 3 : 6-dibromocarbazole by Et_2SO_4—$COMe_2$–60% aq. KOH. (**II**) is prepared from 3-iodo-9-ethylcarbazole by KI–KIO_3–AcOH. (**III**) is smoothly (94%) dehalogenated by Pd–C. Distillation of 2-bromoquinoline (1 mol.) with CuCN (1·5 mol.) gives 78—92% of 2-cyanoquinoline, readily hydrolysed to the acid, m.p. 270—272°, which with NHR_2 and $POCl_3$ at 110° gives *quinoline-3-carboxyldi-methyl-*, b.p. 157—160°/2 mm. (*hydrochloride*, m.p. 191—192°; *picrate*, m.p. 195°), *-ethyl-*, b.p. 190—194°/10 mm. [*hydrochloride*, m.p. 159—160° (decomp.); *picrate*, sinters at 188—190°, m.p. 190—192°], -n-, b.p. 173°/1·5 mm. (*hydrochloride*, m.p. 153—154°; *picrate*, m.p. 159—160°), and -iso*propyl-*, m.p. 81—84°, b.p. 169—170°/1·5 mm. [*hydrochloride*, m.p. 173·5—174·5° (decomp.); *picrate*, m.p. 225—227°], *-amide*. The *piperidide*, m.p. 88—89°, b.p. 198—202°/2·5 mm. [*hydrochloride*, m.p. 122—158° (decomp.); *picrate*, m.p. 195·5—196·5°], is similarly obtained, but the *diallylamide*, b.p. 178—180°/2 mm. (*hydrochloride*, m.p. 152·5—153·5°; *picrate*, m.p. 152—152·5°), is prepared from the acid and amine by P_2O_5. Amides are obtained in only poor yield from the acid chloride. R. S. C.

Synthetical experiments in the group of sympathomimetics. III. S. Rajagopalan (*Proc. Indian Acad. Sci.*, 1941, **14**, **A**, 126—132).—The prep. from compounds derived from C_6H_6,

*iso*quinoline, and phenanthrene of substances containing the group $OH{\cdot}CAr_2{\cdot}CH_2{\cdot}NH_2$ has been effected for pharmacological purposes. $NH_2{\cdot}CH_2{\cdot}CO_2Et$,HCl and Mg 9-phenanthryl bromide in Et_2O–C_6H_6 (in N_2) afford β-hydroxy-ββ-9-phenanthrylethylamine [*hydrochloride*, m.p. 239—240° (decomp.); *picrate*, m.p. 209—210° (decomp.)]. Gradual addition of dil. Na_2CO_3 to $Br{\cdot}[CH_2]_2{\cdot}COCl$ and homoveratrylamine in petrol leads to *β-bromopropionhomoveratrylamide*, m.p. 120—121°, cyclised by $POBr_3$ in $CHCl_3$ at room temp. to 6 : 7-dimethoxy-1-β-bromoethyl-3 : 4-dihydro*iso*quinoline (*picrate*, decomp. 166—168°). *o-β-Bromopropionamidodiphenyl* has m.p. 118°. *ββ-Diphenylpropionamide*, m.p. 124—125°, is converted by NaOCl followed by KOH into ββ-diphenylethylamine [*hydrochloride*, m.p. 256°; *picrate*, m.p. 210° (decomp.)]. MgPhBr and $NH_2{\cdot}CH_2{\cdot}CO_2Et$,HCl give β-hydroxy-ββ-diphenylethylamine [*hydrochloride*, m.p. 191° (decomp.); *picrate*, m.p. 179° (decomp.)]. *β-Hydroxy-ββ-diphenyl-α-benzylethylamine hydrochloride*, m.p. 225—226° (decomp.), is derived analogously from $CH_2Ph{\cdot}CH(NH_2){\cdot}CO_2Et$,HCl. Dibenzylaminomethane [*hydrochloride*, m.p. 200—201°; *N-formyl* derivative, m.p. 88—89°; *picrate*, m.p. 191—192° (decomp.)] could not be prepared by reduction of $(CH_2Ph)_2C{:}N{\cdot}OH$ but is readily derived from the ketone and $HCO{\cdot}NH_2$ at 175—185°. *Diphenylacethomopiperonylamide*, m.p. 139—140°, is cyclised by $POCl_3$ in boiling PhMe to 6 : 7-*methylenedioxy*-1-*benzhydryl*-3 : 4-*dihydro*isoquinoline, m.p. 125—126° after softening at 120°, reduced by Zn dust and dil. H_2SO_4 at 100° to the 1 : 2 : 3 : 4-H_4-*base* [*hydrochloride*, m.p. 239° (decomp.); *N-Ac* derivative, m.p. 172°; *picrate*, m.p. 212—213° (decomp.)]. Similarly, *o-nitrobenzhomoveratrylamide*, m.p. 142°, gives 6 : 7-*dimethoxy*-1-*o-nitrophenyl*-3 : 4-*dihydro*isoquinoline, m.p. 117° after slight softening at 112°, converted into 6 : 7-*dimethoxy*-1-*o-aminophenyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m.p. 162° [*monohydrochloride*, m.p. 189° (decomp.) after softening at 183°; *Ac*$_2$ derivative, m.p. 196°]. H. W.

3 : 3-Bis-(4′-hydroxy-3′-methoxyphenyl)oxindole and some derivatives. E. Bureš and R. Sedlář (*Časopis Československ. Lék.*, 1939, **19**, 93—102).—Condensation of isatin and guaiacol in conc. H_2SO_4 yields the *β-isomeride* (**I**), m.p. 250° (decomp.), and condensation with $ZnCl_2$ at 115° yields the *α-isomeride* (**II**), m.p. 190° (decomp.), of 3 : 3-*bis*-(4′-*hydroxy*-3′-*methoxyphenyl*)*oxindole*. Condensation in H_2SO_4 at a high temp. yields sulphonated (**I**) containing 2·5—3·0% S. From (**I**) are prepared the *Cl*$_8$-, no m.p., *Br*$_3$-, m.p. 280° (decomp.), *Br*$_4$-, no m.p., *Ac*$_2$, m.p. 178°, and *Bz*, m.p. 143°, derivatives, and 3 : 3-*bis*-(3′ : 4′-*dimethoxyphenyl*)*oxindole*, m.p. 148°. With $Hg(OAc)_2$ both (**I**) and its Br_4-derivative give Hg^{II} salts (no m.p.). From (**II**) are prepared the *Cl*$_6$-, m.p. 136° (decomp.), *Cl*$_7$-, m.p. 165° (decomp.), *Cl*$_8$-, no m.p., *Br*$_3$-, m.p. 228° (decomp.), *Br*$_4$-, no m.p., and *I*-, no m.p., -derivatives. F. R.

Selective hydrogenation of derivatives of pyrrole, indole, carbazole, and acridine. H. Adkins and H. L. Coonradt (*J. Amer. Chem. Soc.*, 1941, **63**, 1563—1570).—Selective hydrogenation of heterocyclic rings is improved by substituents which repress resonance; it usually proceeds better in presence of Cu chromite than in presence of Raney Ni. In presence of Raney Ni, 1-phenylpyrrole (**I**) (prep. from NH_2Ph and mucic acid described) gives 1-phenylpyrrolidine, 2-phenylpyrrole (**II**) [prep. by pyrolysis of (**I**)] at 165° gives 2-*cyclo*hexylpyrrolidine (**III**) (15%), b.p. 115—116°/15 mm. (*hydrochloride*, m.p. 163—164°), and unchanged (**II**) (40%); in presence of Cu chromite at 200°, (**II**) gives 55% of (**III**) and 20% of unchanged (**II**). *Et* 2-*phenylpyrrole*-1-*carboxylate* [prep. from the K derivative of (**II**) by $ClCO_2Et$], b.p. 165—166°/19 mm., in presence of Ni at 155° gives *Et* 2-*phenylpyrrolidine*-1-*carboxylate* (80%), b.p. 178—180°/25 mm. (also obtained in presence of Cu chromite), but at 250° gives *Et* 2-cyclo*hexylpyrrolidine*-1-*carboxylate* (83%), b.p. 170—173°/22 mm. 1-Benzylpyrrole (prep. from $CH_2Ph{\cdot}NH_2$ and mucic acid described), m.p. 14—15°, b.p. 122—124°/10 mm., in presence of Ni at 200—260° give 1-benzylpyrrolidine (**IV**), b.p. 234—236°, or pyrrolidine + PhMe, the amount of fission depending on the temp.; in presence of Cu chromite at 200°, 67% of (**IV**) is formed and very little fission occurs. In presence of Cu chromite, indole (prep. from the H_2-derivative by Pd in boiling xylene) at 170°, 2-methyl- at 190°, 3-ethyl- at 160°, and 1 : 2-dimethyl-indole at 170° give, respectively, 2 : 3-dihydro-indole (57%), b.p. 229—231° (obtained also by reducing *o*-$NO_2{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}Br$ by $SnCl_2$–HCl and cyclising the product at 150°), -2-methyl- (**V**) (55%), b.p. 227—230°, -3-*ethyl*- (56%), b.p. 109—110°/7 mm. (*PhSO*$_2$ derivative, m.p. 97—97·5°), and -1 : 2-*dimethyl-indole* (**VI**) (48%), b.p. 227—229°, with corresponding amounts of unchanged material, an equilibrium being probably established. In presence of Ni at 170° (0·5 hr.) 23% of (**V**) is accompanied by 30% of 2-methyloctahydroindole (**VII**), b.p. 191—192°, but at 220—250° 79—81% of (**VII**), octahydroindole, b.p. 68—70°/13 mm., and 3-*ethyloctahydroindole*, b.p. 80—82°/7 mm. (*PhSO*$_2$ derivative, m.p. 51—52°), are obtained; the H_2-derivatives give similarly H_8-derivatives, but (**VI**) is not further affected. Conversion of 2-phenylindole into the 2 : 3-H_2-derivative, m.p. 46—47°, b.p. 184—186°/10 mm., is very facile, occurring (43%) at 155° in presence of Cu chromite, and at 190° approx. equal amounts of 2-cyclo*hexyl-indole* (**VIII**), m.p. 103—105°, and -2 : 3-*dihydroindole*, m.p. 65—67°, b.p. 168—170°/8 mm. [*hydrochloride*, m.p. 202—204°; also obtained from (**VIII**) by Zn–HCl], are formed, probably in equilibrium with each other and probably produced by way of 2-1′ : 2′-dihydrophenylindole; in presence of Raney Ni at 230° 81% of 2-cyclo*hexyloctahydroindole*, b.p. 147—149°/7 mm. (*hydrochloride*, m.p. 290—293°), is formed. In presence of Ni at 230° (15 min.) carbazole (purified by H_2–Ni at 60°/65 mm. in dioxan) gives the 1 : 2 : 3 : 4-H_4- (**IX**) (33%), m.p. 115—115·5°, *cis*-1 : 2 : 3 : 4 : 10 : 11-H_6- (14%), m.p. 98—99° (9-*Ac* derivative, m.p. 97—98°), and H_{12}-derivative (**X**) (14%), m.p. 73—74·5°, b.p. 124—125°/10 mm. (*hydrochloride*, m.p. 208—209°), but after longer heating or at higher temp. only (83, 87%) (**X**) is obtained; in presence of Cu chromite at 220—230° (**IX**) is the main product. 9-Methyl- and -ethyl-carbazole behave similarly, 1 : 2 : 3 : 4-tetrahydro-9-methyl-, m.p. 49—50°, and -ethyl-, b.p. 168—170°, and dodecahydro-9-methyl-, b.p. 126—128°/8 mm., and -ethyl-carbazole, b.p. 124—125°/8 mm., being isolated. In presence of Ni at 25° acridine gives the 9 : 10-H_2-derivative (**XI**) (85%), m.p. 169—169·5°, at 100° gives *s*- (16%), m.p. 73·5—74°, b.p. 163—164°/8 mm., and 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-H_8-derivatives (**XII**) (38%), b.p. 163—164°/8 mm., and $\Delta^{11:12}$-*dodecahydroacridine* (**XIII**) (22%), m.p. 63·5—64·5°, and at 240° gives tetradecahydroacridine (81%), m.p. 90·5—91·5°, b.p. 138—139°/11 mm. (*hydrochloride*); in presence of Cu chromite at 150° it gives (**XI**) (90%) and at 190° gives (**XII**) (70%) and (**XIII**) (13%). R. S. C.

4-(or 5-)Aminoglyoxaline. G. Hunter and J. A. Nelson (*Canad. J. Res.*, 1941, **19**, **B**, 296—304; cf. A., 1936, 999).—4-(or 5-)Nitroglyoxaline (**I**) and $SnCl_2$,H_2O–Ac_2O–HCl–AcOH, in N_2, at 90°, give a solution from which is obtained by quick and careful treatment 4-(or 5-)*acetamidoglyoxaline*, m.p. 226° (picrate, m.p. 208°; flavianate, m.p. 260°) (acid hydrolysis causes fission of ring). (**I**) and Na–Hg–MeOH at 0° (in N_2), followed by $Hg(OAc)_2$, give a Hg salt, decomposed by HCl in MeOH to give 4-(or 5-)*aminoglyoxaline dihydrochloride*, m.p. 184° (corresponding *sesquipicrate*, m.p. 194°). The free base is highly reactive and is unstable in aq. media. A. T. P.

1-Aryl-5-methyl-3-pyrazolones.—See B., 1942, II. 6.

Ethylenediamine. V. Action of aromatic acid chlorides on 4 : 5-dihydro-iminazoles [-glyoxalines] in aqueous media. S. R. Aspinall (*J. Org. Chem.*, 1941, **6**, 895—901).—Hydrolysis of 2-methyl-4 : 5-dihydroglyoxaline (**I**) by boiling H_2O proceeds readily with quant. formation of $NH_2{\cdot}[CH_2]_2{\cdot}NHAc$, isolated as the picrate. 2-Phenyl-4 : 5-dihydroglyoxaline (**II**) is much more slowly hydrolysed and gives $NH_2{\cdot}[CH_2]_2{\cdot}NHBz$. Alternate additions of BzCl and saturated aq. Na_2CO_3 to (**I**) in H_2O at 0° lead to $NHBz{\cdot}[CH_2]_2{\cdot}NAcBz$ (**III**). Similarly treatment of (**II**) in EtOH gives $NHBz{\cdot}[CH_2]_2{\cdot}NBz_2$ (**IV**) and an unidentified compound, m.p. 122°. (**IV**) is hydrolysed by KOH in 50% EtOH at room temp. to $(CH_2{\cdot}NHBz)_2$ and BzOH, whereas (**III**) under similar conditions yields $(CH_2{\cdot}NHBz)_2$ and $NHAc{\cdot}[CH_2]_2{\cdot}NHBz$. Alternate addition of $PhSO_2Cl$ and 10% Na_2CO_3 to (**I**) in H_2O at 0° gives $SO_2Ph{\cdot}NH{\cdot}[CH_2]_2{\cdot}NAc{\cdot}SO_2Ph$ (**V**), whilst (**II**) similarly yields $SO_2Ph{\cdot}NH{\cdot}[CH_2]_2{\cdot}NBz{\cdot}SO_2Ph$ (**VI**). (**V**) is hydrolysed by 10% NaOH at room temp. to AcOH and $(CH_2{\cdot}NH{\cdot}SO_2Ph)_2$; (**VI**) behaves similarly. 4 : 5-Dihydroglyoxalines react with acid chlorides in caustic alkaline media to yield the same products in the same yields as result from their stepwise treatment with alkali carbonate followed by alkali hydroxide. H. W.

Synthesis of 3-β-hydroxyethylpyrimidines and a 3-β-hydroxyethyluric acid. A. H. Nathan and M. T. Bogert (*J. Amer.*

Chem. Soc., 1941, **63**, 2567—2569).—CN·CH_2·CO_2Et, OH·$[CH_2]_2$·NH·CO·NH_2, and NaOEt in boiling EtOH give *4-imino-3-β-hydroxyethylbarbituric acid* (71%), decomp. 256° (partial melting), converted by *iso*-C_5H_{11}·O·NO (not $NaNO_2$) in boiling 45% EtOH into *4-imino-3-β-hydroxyethylvioluric acid* (90%), darkens at >200° (NH_4 salt), which is reduced by $Na_2S_2O_4$-aq. NH_3 to 4 : 5-*diamino-3-β-hydroxyethyluracil* (87%), m.p. 253—254°. With $CO(NH_2)_2$ at 170—180° this yields *3-β-hydroxyethyluric acid*, decomp. 315—325°, which is more sol. in H_2O than is uric acid. M.p. are corr.

R. S. C.

5-Hydroxy-2-methylbenziminazole. S. D. Gershon and G. L. Webster (*J. Amer. Chem. Soc.*, 1941, **63**, 2853).—3 : 4 : I-$(NHAc)_2C_6H_3$·OAc in boiling conc. HCl–EtOH or 3 : 4 : I-NH_2·$C_6H_3(NHAc)$·OAc in boiling 25% aq. HCl gives *5-hydroxy-2-methylbenziminazole*, m.p. (+H_2O) 187—188°, (anhyd.) 187·5—188·5°. R. S. C.

Cyanogen halides.—See A., 1942, I, 110.

Di(acylamino)-1 : 3 : 5-triazines.—See B., 1942, II, 6.

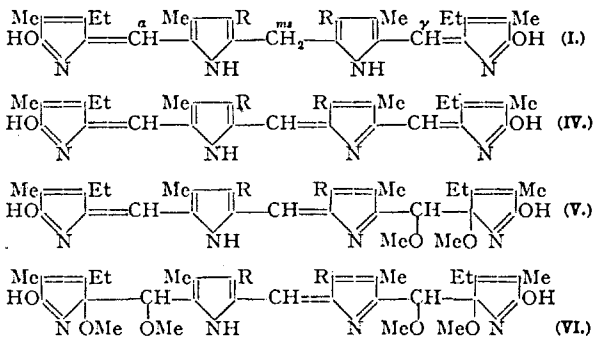
New indigoid pigment formed from the glyoxaline nucleus. G. Hunter and I. Hlynka (*Canad. J. Res.*, 1941, **19**, **B**, 305—309).—4-(or 5-)Nitroglyoxaline after reduction by Na–Hg in MeOH and acidification affords a blue pigment, probably 4 : 4′-*di*(*glyoxal-5-one*) $\left(CH\ll^{NH—CO}_{N—C:}\right)_2$ (contains the indigoid nucleus), formed probably through 4-(or 5-)hydroxyglyoxaline, which tautomerises to the glyoxalone : this on oxidation condenses to give the pigment. Guanidinoglyoxaline dihydrochloride and $Cu(OH)_2$-aq. Na_2CO_3 at 100° (bath) afford, through the respective Cu and Ag salts, a small amount of unstable 5 : 5′-dihydroxy-4 : 4′-diglyoxaline (leuco-form of pigment). A. T. P.

Effects of ultra-violet radiation on sodium thymonucleate.—See A., 1942, III, 264.

Light absorption and constitution of chlorophyll derivatives. Absorption of the dihydroxy-compounds.—See A., 1942, I, 82.

Mechanism of Gmelin's reaction. I. Mesobilipurpurin. W. Siedel and W. Fröwis. **II. Formation and constitution of mesobilipurpurin and mesocholetelin. Modified Gmelin's reaction.** W. Siedel and E. Grams (*Z. physiol. Chem.*, 1940, **267**, 37—48, 49—78).—I. Mesobilirubin XIIIα Me_2 ester (**I**), oxidised by HNO_3–HNO_2 until the resulting solution shows strong absorption in the red and chromatographed yields cryst. *mesobilipurpurin XIIIα Me_2* ester (622 mμ.) (**II**), $C_{35}H_{42}O_7N_4$, m.p. 157—160° (corr.), which in neutral solution has absorption bands at 535 and 496 mμ., in dil. HCl (violet colour) at 586 mμ., as Zn complex in MeOH (blue colour, intense red fluorescence) at 622 mμ., and as Cu complex (green-blue colour, more stable than Zn complex to 5% HCl) at 643 mμ. A second fraction, re-adsorbed on Al_2O_3 and developed with $CHCl_3$–Et_2O, yielded *mesobilipurpurin XIIIα Me_2* ester (630 mμ.) (**III**), with absorption bands at 570 mμ. for the neutral solution and at 630 and 575 mμ. (weak) for the Zn complex. The reactions of (**II**) with I, $FeCl_3$–HCl, etc. indicate that the glaucobilin produced in Gmelin's reaction is converted into (**II**) by a unilateral oxidation of the mol. and a rearrangement of the double linking, the γ-·CH· becoming a γ-·CO· bridge (cf. A., 1941, II, 380). Further action of HNO_3–HNO_2 on (**II**) gives mesocholetelin XIIIα.

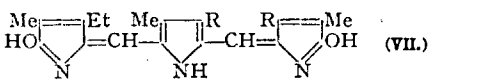
II. Xanthobilirubic acid Me ester with $Pb(OAc)_4$ in AcOH and treatment of the $CHCl_3$-sol. product with $FeCl_3$ affords ferrobilin XIIIα Me_2 ester, converted by 2N-NaOH into glaucobilin XIIIα Me_2 ester (**IV**) (*Cu*^{II} complex salt); with MeOH–HCl, the $CHCl_3$-sol. product gives (**I**) [dihydrochloride, m.p. 237° (corr.)]. (**IV**), treated with HNO_3–HNO_2, gives a reddish-violet $CHCl_3$ extract which, after removal of unchanged (**IV**), yields *mesobilipurpurin XIIIα Me_2* ester (619 mμ.), m.p. 189° (corr.) [which gives a blue-coloured solution in EtOH–$Zn(OAc)_2$ (no fluorescence) with absorption bands at 619 and 670 mμ.], and (**II**). HNO_3–HNO_2 gives a complicated Gmelin's reaction, which can be produced more simply by treatment with dil. Br solution. Thus (**IV**) with Br in $CHCl_3$–MeOH gives mesobilipurpurin XIIIα Me_2 ester (627 mμ.) (**V**), m.p. 219—220° (corr.) [free *acid*, m.p. 187° (corr.), reduced (Na–Hg) to (?) mesobilirubinogen XIIIα, which is converted into ferrobilin and then (**IV**) as above]; (**V**), on repetition of the process, affords the *Me$_4$ ether* of mesocholetelin XIIIα Me_2 ester (**VI**), m.p. 178—180° (corr.) [$Zn(OAc)_2$ gives absorption band at 515 mμ.].



(R = ·$[CH_2]_2$·CO_2Me)

[Colour change of (**I**) → (**IV**) → (**V**) → (**VI**) is yellow (→ green) → blue (→ violet) → red (→ orange) → yellow.]

(**IV**) with $CHCl_3$–Br in presence of H_2O affords, by chromatographing, various mesobilipurpurins, including (**III**) [which is formed from (**IV**) by introduction of OH and OMe groups], (**II**), *mesobilipurpurin XIIIα Me_2* ester (626 mμ.), m.p. 185° (corr.), and a substance, m.p. 174° (corr.) [$Zn(OAc)_2$ gives absorption bands at 621·5 and (weak) 569 mμ.]. Oxidation of (**IV**) by AcOH–Br affords no cryst. product, but that by C_5H_5N–Br, followed by chromatographing, yields a substance, m.p. 160° (decomp.), giving with $Zn(OAc)_2$ no fluorescence and a weak absorption band at 624 mμ. 5-Aldehydo-2-carboxy-3-methylpyrrole-4-propionic acid with Br yields the 2-*Br*-derivative, m.p. 162° (uncorr.), which, condensed with ncoxanthobilirubic acid in HBr–MeOH, gives *Me$_2$ 6′-bromo-1′-hydroxy-1 : 3 : 6-trimethyl-2-ethyltripyrrodiene*(2′α, 4′β)-4 : 5-*dipropionate*, m.p. 195° (corr.), converted by KOAc–AcOH at the b.p. into the corresponding 1′ : 6′-(*OH*)$_2$-compound (**VII**), m.p. 153—154° (corr.); the yellow colour and lack of fluorescence



(R = ·$[CH_2]_2$·CO_2Me)

with $Zn(OAc)_2$ of (**VII**) show that the violet product of Gmelin's reaction is not due to dihydroxytripyrrene formation. The bearing of the above experiments on the course of Gmelin's reaction is discussed and a modification of Fischer and Halbach's structural formula for stercobilin (A., 1936, 346) is advanced. All m.p. under microscope. F. O. H.

Chemically marked antigens. III. Introduction of polycyclic ring systems into proteins. H. Lettré, K. Buchholz, and M. E. Fernholz (*Z. physiol. Chem.*, 1940, **267**, 108—114; cf. A., 1941, II, 363).—Pyrene-3-aldehyde with hippuric acid and NaOAc–Ac_2O at 110° yields *α-benzamido-β-3-pyrenylacrylic acid azlactone* (**I**), m.p. 262°, reduced (HI–red P in Ac_2O) to *3-pyrenylalanine*, m.p. 258° (decomp.). (**I**) in C_5H_5N with 2N-NaOH gives *α-benzamido-β-3-pyrenylacrylic acid*, m.p. 262° [probably with formation of (**I**)] (*Et* ester, m.p. 189—190°), reduced (Na–Hg) to *α-benzamido-β-3-pyrenylpropionic acid*, m.p. 250° (*oxazolone*, m.p. 174°; *Me* ester, m.p. 155—156°). Alanine in aq. K_2CO_3 with 3-pyrenoyl chloride affords *3-pyrenoylalanine*, m.p. 233—235° (*oxazolone*, m.p. 173°; *Me* ester, m.p. 174—175°). The above preps. indicate the possibility of introducing polycyclic systems into the protein mol. by the oxazolone method. F. O. H.

Oxidation–reduction equilibrium, over the whole p_H range, of oxonine and related dyes. L. Michaelis and S. Granick (*J. Amer. Chem. Soc.*, 1941, **63**, 1636—1643).—Absorption spectra show formation of semiquinone radicals in alkaline as well as in acid solution. Measurements for oxonine at both ends of the p_H scale (cf. A., 1941, II, 332) and extrapolation for intermediate p_H determine the consts. of semiquinone formation from p_H −8 to +14, the results agreeing with titration curves. The behaviour of thiazine dyes is discussed.

R. S. C.

Pyronine dyes derived from succinic acid. S. Dutt (*Proc. Indian Acad. Sci.*, 1941, **14**, **A**, 158—164).—Condensation of (·CH_2·CO)$_2$O with the requisite phenol or amine gives the

following -succineins: *o*-cresol-, m.p. 264° (*anhydride*, m.p. 178—179°); *m*-cresol-, m.p. 146°; α-naphthol-, m.p. 245°; *resorcinol*-, m.p. 234°; pyrocatechol-, m.p. 286°; *quinol*, m.p. 258°; pyrogallol-, m.p. 276°; *phloroglucinol*-, m.p. >290°; *m*-aminophenol-, m.p. 224°; m-*dimethylaminophenol*- (*hydrochloride*), m.p. 225—230°; *m*-phenylenediamine-, m.p. 242°. The colours and absorption max. in EtOH and alkali are tabulated and the results are contrasted with those of Dass and Tewari (A., 1941, II, 202). H. W.

Synthesis of *cyclo*hydrazides of coumarone-1 : 2-, thionaphthen-2 : 3-, and indole-2 : 3-dicarboxylic acids. E. H. Huntress and W. H. Hearon (*J. Amer. Chem. Soc.*, 1941, **63**, 2762—2766).—The prep. of benzfuran-1 : 2-dicarboxylic acid, m.p. 248—249° [lit. 259—260° (corr.)], from isatin (Titov *et al.*, A., 1937, II, 512) is improved to give 30·5% over-all yield. The Et_2 ester, m.p. 61—62°, with N_2H_4–EtOH gives the cyclic *hydrazide* (*A*), enolic (**I**), m.p. 280—282°, and keto-*form* (**II**), m.p. 316—318°, also obtained from the acid by 87% $N_2H_4.H_2O$ at 200°. (**I**) gives a purple $FeCl_3$ colour and with CH_2N_2 gives a *Me ether*, m.p. 161—163°, but does not affect ammoniacal $AgNO_3$. Dissolution of (**I**) in alkali and then acidification gives (**II**). (**I**) and (**II**) give the same *Ac* derivative, m.p. 224—226°. *Thionaphthen-2 : 3-dicarboxylhydrazide* (**III**), sinters at ~350°, m.p. 360—361° (*Ac* derivative, m.p. 195—196°), is obtained similarly from the Et ester in EtOH–H_2O at 100°, the acid in aq. NaOAc at 160±5°, or the anhydride in warm H_2O. *Indole-2 : 3-dicarboxylhydrazide* (**IV**), m.p. >360° (*Ac* derivative, decomp. >~270°), is similarly prepared from the Me_2 ester. (*A*), (**III**), and (**IV**) react as enols with Ac_2O and $FeCl_3$ (but not $AgNO_3$) and are titrated as monobasic acids with aq. alkali. R. S. C.

Reduction of the *o*-nitrophenyl esters of certain acids. L. C. Raiford and W. G. Huey (*J. Org. Chem.*, 1941, **6**, 858—866).—2 : 4 : 1-NO_2·C_6H_3Br·OH is converted by alkali hydroxide and the requisite alkyl chloroformate into 4-*bromo*-2-*nitrophenyl Me*, m.p. 61—63°, Et, m.p. 77°, *Pr*$^{\alpha}$, m.p. 49—51°, and *Bu*$^{\alpha}$, b.p. 181°/5—6 mm., *carbonate*. These compounds are finely ground, mixed with conc. HCl, and gradually treated with Sn at <20°. In each case the 2-NH_2-derivative is isolated and its direct rearrangement to the isomeric 2-hydroxyphenylurethane is observed. The latter is stable under the experimental conditions. The *hydrochlorides* of the 4-bromo-2-aminophenyl Me, Et, Pr$^{\alpha}$, and Bu$^{\alpha}$ carbonates have m.p. 147—148°, 141—143°, 136°, and 138° respectively. The 4-*bromo*-2-*carboalkoxyaminophenols* have m.p. 168°, 141°, 113—114°, and 121—123° when Alk = *Me*, Et, *Pr*$^{\alpha}$, and *Bu*$^{\alpha}$ respectively. Benzoxazolone, furoyl chloride, and C_5H_5N afford 1-*furoylbenzoxazolone*, m.p. 141—143°. 5-Bromofuroic acid, m.p. 190—191° (corresponding *chloride*, b.p. 89°/8 mm., m.p. 54—56°, and *anilide*, m.p. 145°), is obtained in 54% yield by the action of Br vapour on finely-divided furoic acid at 100°. The following *furoates* are described: o-*nitrophenyl* (**I**), m.p. 83—84°; 4-*bromo*-2-*nitrophenyl*, m.p. 88—89°; 4 : 6-*dibromo*-2-*nitrophenyl*, m.p. 133—134°; 4-*bromo*-2-*nitro*-m-*tolyl*, m.p. 74—76°; also 4-*bromo*-2-*nitrophenyl* 5-*bromofuroate*, m.p. 135°. Reduction of (**I**) at 0° gives mainly 2-2′-*furylbenzoxazole*, m.p. 83—85°. When 1 Br is present in the Ph residue some 5-*bromo*-2-2′-*furylbenzoxazole*, m.p. 92—93°, is obtained but the chief product is 4-*bromo*-2-*furoamidophenol*, m.p. 238°. With the Br_2-compound only 4-*bromo*-2-5′-*bromofuroamidophenol*, m.p. 282—284° (decomp.), could be isolated. 5-*Bromo*-2-2′-*furyl*-6-*methylbenzoxazole*, m.p. 122—124°, and 4-*bromo*-2-*furoamido*-m-*cresol*, m.p. 239—240°, are described. H. W.

[Sulphanilamido]thiazolones. M. L. Moore and C. S. Miller (*J. Amer. Chem. Soc.*, 1941, **63**, 2781—2784).—Condensation of *p*-NHAc·C_6H_4·SO_2Cl (**I**) with the appropriate 2-amino-4-thiazolone, best in C_5H_5N, and subsequent acid hydrolysis gives 2-*sulphanilamido*-4-*thiazolone*, m.p. 235—238° [N^4-*Ac* derivative (**II**), m.p. 266·5°], 2-*sulphanilamido*-5-*methyl*-, m.p. 167—168° (N^4-*Ac* derivative, m.p. 244—245°), -5-*ethyl*- (**III**), m.p. 184—184·5° [N^4-*Ac* derivative (**IV**), m.p. 200—201°], -5-n-*propyl*- (**V**), m.p. 160—161° (N^4-*Ac* derivative, m.p. 187—188°), -5-n-*butyl*- (**VI**), m.p. 206·5—207·5° (N^4-*Ac* derivative, m.p. 184—185°), -5-n-*amyl*- (**VII**), m.p. 167—168° (N^4-*Ac* derivative, m.p. 190—191°), -5-n-*hexadecyl*-, m.p. 129—131° (N^4-*Ac* derivative, softens at 130°, m.p. up to 143°), -5 : 5-*dimethyl*- (**VIII**), m.p. 210—211° (N^4-*Ac* derivative, m.p. 247—248°), and -5 : 5-*diethyl*- (**IX**), m.p. 198—199° (N^4-*Ac* derivative, m.p. 210—211·5°), -4-*thiazolone*. *p*-C_6H_4X·SO_2Cl gives similarly 2-N^4-n-*hexoyl*-, m.p. 174—175°, and 2-N^4-n-*heptoyl*-*sulphanilamido*-5-*ethyl*-4-*thiazolone*, m.p. 140—141°, 2-N^4-n-*hexoyl*- (**X**), m.p. 134—135°, and 2-N^4-n-*heptoyl*-*sulphanilamido*-5-n-*butyl*-4-*thiazolone* (**XI**) m.p. 139—140°, 2-p-*nitrobenzenesulphonamido*-5-*ethyl*-, m.p. 192—193°, and -5-*butyl*-4-*thiazolone*, m.p. 186—187°, and 2-p-*toluenesulphonamido*-5-*ethyl*-4-*thiazolone*, m.p. 139—140°. Addition of CH_2Cl·COCl or CHEtBr·COBr to (**I**) in N-NaOH gives N^4-*acetyl*-N^1-α-*chloroacetyl*-, m.p. 241—242° (decomp.), and -N^1-α-*bromobutyryl*-*sulphanilamide*, m.p. 230—232° (decomp.), converted by KCNS in boiling EtOH into (**II**) and (**IV**), respectively. The antistreptococcal activity of (**V**), (**VI**), (**VII**), (**X**), and (**XI**), the antipneumococcal activity of (**III**), (**VI**), (**VIII**), (**IX**), and (**X**), and the antistaphylococcal activity of (**III**) and (**IX**) are promising. R. S. C.

4 : 4-Dimethylthiopheno[2, 3-*b*]pyridine, an isosteride of 2 : 4-dimethylquinoline. W. S. Emerson, F. W. Holly, and L. H. Klemm (*J. Amer. Chem. Soc.*, 1941, **63**, 2569—2570).—Heating 2-aminothiophen stannichloride with CH_2Ac_2 at 100° and cyclising the crude product by conc. H_2SO_4 at 25° or $ZnCl_2$ or P_2O_5 in boiling xylene gives 4 : 6-*dimethylthiopheno*-2′ : 3′-2 : 3-*pyridine* (80%), b.p. 103—108°/4 mm. [*hydrochloride*, m.p. 241—242° (decomp.); *methiodide*, m.p. 228—229° (decomp.); *picrate*, m.p. 190—191°], converted by PhCHO and $ZnCl_2$ at 25° into the 4 : 6-*distyryl* compound, m.p. 238° (*hydrochloride*, m.p. 268°). The Doebner–Miller reaction and attempts to prepare similar compounds failed. R. S. C.

N^1-Heterocyclic sulphanilamide derivatives. G. W. Raiziss, L. W. Clemence, and M. Freifelder (*J. Amer. Chem. Soc.*, 1941, **63**, 2739—2740).—Condensation of *p*-NHAc·C_6H_4·SO_2Cl with the requisite amine in C_5H_5N, C_5H_5N-$COMe_2$, or $NaHCO_3$–H_2O–$COMe_2$ and subsequent hydrolysis by N-NaOH or 10% HCl gives 5-*sulphanilamido*-2-*methoxy*-, m.p. 178°, and 2-*sulphanilamido*-6-*piperidino*-*pyridine*, m.p. 185°, 1-*sulphanilamido*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m.p. 125°, 7-*sulphanilamido*-2-*hydroxy*-3 : 4-*dihydroquinoxaline*, m.p. 188°, 2-*sulphanilamido*-5 : 6-*diphenyl*-1 : 3 : 4-*triazine*, m.p. 189° after sintering, 2-*sulphanilamido*-5 : 6-*dihydro*-, m.p. 88°, and -5-*bromo*-5 : 6-*dihydro*-*thiazine*, m.p. 100°, 3-*sulphanilamido*-5-*methyltriazole Na* salt, m.p. >300°, 4-*sulphanilamido*-, m.p. 185°, and 4-*sulphanilamido*-3 : 5-*dimethyl*-*pyrazole*, m.p. 233°, 2-*sulphanilamido*-*benziminazole*, m.p. 211—212°, -*phenothiazine*, m.p. >315°, -*pyrazine* (**I**), m.p. 253°, and -*thiazoline* (**II**), m.p. 209—210°, 4-*sulphanilamido*-3 : 5-*diphenylpyrrole*, m.p. 178—180°, and 5-*sulphanilamidohydantoin* (**III**), m.p. 209—210°. Of these products, only (**I**), (**II**), and (**III**) show therapeutic promise. R. S. C.

Preparation and bioassay of aneurin hydriodide. J. G. Tolpin, J. R. Foy, and L. R. Cerecedo (*J. Amer. Chem. Soc.*, 1941, **63**, 2848).—Na converts aneurin chloride hydrochloride (**I**) in AcOH containing a trace of H_2O into the free base, whence HI yields *aneurin iodide hydriodide*, m.p. 230—231°, which is biologically more potent than (**I**). R. S. C.

VII.—ALKALOIDS.

Quantitative separation of ergometrine from other ergot alkaloids. D. C. Grove (*J. Amer. Pharm. Assoc.*, 1941, **30**, 260—262).—The alkaloid mixture, dissolved in 1% aq. tartaric acid and made slightly alkaline with aq. NH_3, is repeatedly extracted with Et_2O; the extract is then repeatedly extracted with dil. aq. NH_3. The aq. residue and the aq. NH_3 washings are combined and freed from dissolved Et_2O and the alkaloid content is determined colorimetrically. The method gives a recovery of ergometrine of 98—99%, whilst only ~5% of the ergometrinine present is retained by the aq. extracts. F. O. H.

Erythrina **alkaloids. X. Isolation and characterisation of erysonine and other liberated alkaloids.** K. Folkers, J. Shavel, jun., and F. Koniuszy (*J. Amer. Chem. Soc.*, 1941, **63**, 1544—1549; cf. A., 1940, II, 332).—Erysopine and hypaphorine are isolated from seeds of *Erythrina crista-galli*, L., *E. costaricensis*, Micheli (**I**), *E. subumbrans* (Hassk.), Merr., *E. Dominguezii*, Hassler, *E. macrophylla*, DC., *E. acanthocarpa*, E. Mey (**II**), *E. rubrinervia*, H.B.K. (**III**), *E. senegalensis*, DC., and *E. fusca*, Lour. All except (**II**) and (**III**) yield also erysodine. Some varieties of (**I**) yield also *erysonine*, $C_{17}H_{19}O_3N$, m.p. variable, 236—237° to 241—243°

(decomp.), $[\alpha]_D^{25}$ +285° to +289° in 0·5% HCl, +272° in morpholine, which is sol. in dil. NaOH but gives no $FeCl_3$ colour, contains 1 OMe but no NMe or CMe, is unchanged by chromatography, and has curare-like action (intralymphatic injection; frogs) in doses of 100 mg. per kg. The yields of liberated alkaloids generally exceed those of the free alkaloids. R. S. C.

Erythrophleum **alkaloids. V. Identification of the acid of low mol. wt. obtained from conmingine.** L. Ruzicka, G. Dalma, B. G. Engel, and W. E. Scott (*Helv. Chim. Acta*, 1941, **24**, 1449—1458; cf. A., 1941, II, 206).—Coumingine (**I**) is the ester of cassaine with $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$ (**II**). The unexplained sixth O of the (**I**) mol. is derived from the OH of the β-hydroxy*iso*valeryl residue. The previous mol. formula $C_{28}H_{45}O_6N$ for (**I**) must be replaced by $C_{29}H_{47}O_6N$. Correspondingly coumingic acid is $C_{25}H_{38}O_6$, not $C_{24}H_{36}O_6$. The isolation of homogeneous (**II**) or of its Me ester from (**I**) is very difficult. The following compounds are described: *p-phenylphenacyl* ester, m.p. 85—86°, of synthetic (**II**) and of (**II**) derived from (**I**), m.p. 135°, of *dl*-$OH{\cdot}CHEt{\cdot}CO_2H$, m.p. 172—173°, of $OH{\cdot}CMe_2{\cdot}CO_2H$, m.p. 108—109°, of $OH{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$ and, m.p. 87—88°, of $OH{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H$ (**III**); *hydrazide*, m.p. 102—103°, of (**II**) and its condensation *product*, m.p. 114—115°, with COPhMe; *hydrazides*, m.p. 115—116°, of (**III**) and its condensation *product*, m.p. 142—143°, with COPhMe. M.p. are corr. H. W.

VIII.—ORGANO-METALLIC COMPOUNDS.

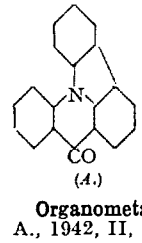
Arsonium compounds. III, IV. F. F. Blicke and S. R. Safir (*J. Amer. Chem. Soc.*, 1941, **63**, 1493—1496, 1496—1498; cf. A., 1939, II, 130).—III. $AsPhMe_3I$ in H_2O with Ag_2O and then HNO_3 gives the nitrate, m.p. 194—196°, which with H_2SO_4–HNO_3 (*d* 1·6) gives m-*nitrophenyltrimethylarsonium nitrate*, m.p. 278—279° (decomp.), converted by aq. NaI into the *iodide*, m.p. 286—290° (decomp.), and thence by Ag_2O and later HCl into the *chloride*, m.p. 263—270° (decomp.). Reduction by $SnCl_2$–HCl–AcOH and then treatment with NaOH and NaI gives m-*aminophenyltrimethylarsonium iodide*, m.p. 175—176° [*Ac* derivative, m.p. 242—246° (decomp.)]. The derived *chloride* (**I**), m.p. 243—244° (decomp.) [*Ac* derivative, m.p. 256—258° (decomp.)], affords (diazo-reaction etc.) m-*hydroxyphenyltrimethylarsonium iodide*, m.p. 208—211° (decomp.). *p*-$C_6H_4Br{\cdot}AsMe_2$ and boiling MeI give p-*bromophenyltrimethylarsonium iodide*, m.p. 253—255° (decomp.), and thence, as above, the corresponding *nitrate*, m.p. 163—165°, and 4-*bromo*-3-*nitrophenyltrimethylarsonium nitrate* (**II**), m.p. 176—181° (decomp.). With aq. NaBr this gives the *bromide*, m.p. 255—275° (decomp.), which in boiling aq. KOH (later neutralisation by HBr) gives 3-*nitro*-4-*hydroxyphenyltrimethylarsonium bromide*, m.p. 269—271° (decomp.) [corresponding *nitrate*, m.p. 225° (decomp.)], and thence 3-*amino*-4-*hydroxyphenyltrimethylarsonium chloride hydrochloride* (**III**), m.p. 211—215° (decomp.). Reduction of (**II**) gives 4-*bromo*-3-*aminophenyltrimethylarsonium iodide*, m.p. 235—237° (decomp.). (p-$C_6H_4Br)_2AsMe$ gives similarly *di*-p-*bromophenyldimethylarsonium iodide*, m.p. 221—224°, and *nitrate*, m.p. 195—196°, and *di*-4-*bromo*-3-*nitrophenyldimethylarsonium nitrate*, m.p. 206—207°, *bromide*, m.p. 183—185° (decomp.), and *iodide*, m.p. 169—170° (decomp.) (also obtained from the arsine and MeI). (**I**) and (**III**), respectively, have min. toxic dose 30 and 70—80 mg. per kg. body wt. The min. lethal dose of (**I**) is 40 mg. per kg. There is no trypanocidal action by (**I**) at 10 or (**III**) at 50 mg. per kg. and no germicidal action by (**III**) in 1% solution at p_H 2·07.

IV. $AsPh_3Me{\cdot}NO_3$ affords *tri*-m-*nitrophenylmethylarsonium chloride*, softens at 80°, foams at 100°, decomp. complete at 130°, and *tri*-m-*aminophenylmethylarsonium chloride*, m.p. 198—200° [*Ac* derivative, m.p. 181—190° (decomp.)], and *iodide*, m.p. 167—169°. (m-$OMe{\cdot}C_6H_4)_3As$ and MeI give *tri*-m-*anisylmethylarsonium iodide*, m.p. 120—121°. (p-$C_6H_4Br)_3As$ gives *tri*-p-*bromophenylmethylarsonium iodide*, m.p. 178—180°, and *nitrate*, +H_2O, softens at 91—105° (? loss of H_2O), m.p. 187—195° (decomp.), and *tri*-4-*bromo*-3-*nitrophenylmethylarsonium nitrate*, m.p. 175—177° (decomp.). $AsPh_4{\cdot}NO_3$ gives *tetra*-m-*nitrophenylarsonium nitrate*, m.p. 248—256°, *chloride* (dried at 160°; ? loss of EtOH), m.p. 235—239° (decomp.), *bromide*, m.p. 252—258° (decomp.), and *iodide*, m.p. 235—237°, and *tetra*-m-*aminophenylarsonium chloride* (**IV**), m.p. >325° [*Ac* derivative, m.p. 172—220° (decomp.)], and *bromide*, m.p. 325°. The min. lethal and toxic doses of (**IV**) are 30 and 20 mg. per kg., respectively; there is no trypanocidal action at 10 mg. per kg. R. S. C.

Organo-phosphorus compounds. I. Derivatives [prepared from] 4-chloro-3-nitrophenylphosphinic acid. G. B. Arnold and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1941, **63**, 2637—2639).—p-$C_6H_4Cl{\cdot}PO_2H_2$ (prep. modified; cf. Michaelis, A., 1897, i, 48; 10% yield) and HNO_3 (*d* 1·52) at 100° give 3 : 4 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}PO_3H_2$ (**I**) (90%; cf. *loc. cit.*), m.p. 166°, the Na_1 salt of which with the appropriate amine in H_2O at 120° gives 3-*nitro*-4-n-*propyl*-, m.p. 178—179° (decomp.), -4-n-, m.p. 176—178° (decomp.), and -4-iso-*butyl*-, m.p. 176—180° (decomp.), -4-n-, m.p. 132—134°, and -4-iso-*amyl*-, m.p. 171—173° (decomp.), and -4-β-*hydroxyethyl*-, m.p. 182° (decomp.), -*aminophenylphosphinic acid* and 3-*nitro*-4-*morpholinophosphinic acid*, m.p. 176°. Hydrogenation (Raney Ni; 40 lb.) of the Na_1 salts of the NO_2-acids in H_2O gives 3-*amino*-4-n-*propyl*-, -4-n- and -4-iso-*butyl*-, -4-n- and -4-iso-*amyl*-, and -4-β-*hydroxyethyl*-*aminophenylphosphinic acid* and 3-*amino*-4-*morpholinophenylphosphinic acid*, which behave as amine salts, all having m.p. >200°. Glycine, (**I**), and K_2CO_3 in *iso*-$C_5H_{11}{\cdot}OH$ at 145° give 3-*nitro*-4-*carboxymethylaminophenylphosphinic acid*, m.p. >200°, which with H_2–Raney Ni in aq. NaOH (1 mol.) gives, by reduction and elimination of H_2O, 3-*keto*-1 : 2 : 3 : 4-*tetrahydro*-6-*quinoxalinylphosphinic acid*, m.p. >200°. With PhOH, K_2CO_3, and a trace of Cu powder at 125°, (**I**) gives 3-*nitro*-4-*phenoxyphenylphosphinic acid*, m.p. >200°; 3-*nitro*-4-o- and -p-*chlorophenoxyphenylphosphinic acid*, m.p. >200°, are prepared similarly in *iso*-$C_5H_{11}{\cdot}OH$ at 145°. Hydrogenation as above gives 3-*amino*-4-*phenoxy*-, -4-o- and -p-*chlorophenoxy-phenylphosphinic acid*, (all) m.p. >200°. In boiling 4N-NaOH, (**I**) gives 3-*nitro*-, m.p. 214—216°, and thence 3-*amino*-4-*hydroxyphenylphosphinic acid*, m.p. >200°. R. S. C.

Hexa*cyclo*hexoxydisiloxane, $[(C_6H_{11}O)_3Si]_2O$. W. C. Schumb and D. F. Holloway (*J. Amer. Chem. Soc.*, 1941, **63**, 2853—2854).—This *compound*, m.p. 217·1—217·6°, is prepared by adding *cyclo*hexanol to Si_2OCl_6 in Et_2O and then boiling for 8 hr. R. S. C.

Monometallation of 9-phenylcarbazole. H. Gilman, C. G. Stuckwisch, and A. R. Kendall (*J. Amer. Chem. Soc.*, 1941, **63**, 1758—1759).—9-Phenylcarbazole with $LiBu^a$ and later CO_2 in Et_2O gives, abnormally, 9-phenylcarbazole-2′-carboxylic acid (6·3%), m.p. 182—184° (Me ester, m.p. 139—140°), the acid chloride (PCl_5–xylene) of which is cyclised by $SnCl_4$ in xylene at 0° to 8-*indolo*[3 : 2 : 1-*de*]*acrid*-8-*one* (*A*) (70%), m.p. 180—181° (*oxime*, m.p. 175—176°).



(*A*.)

R. S. C.

Organometallic derivatives of carbazole and quinoline.—See A., 1942, II, 114.

Reactions of chloroamine with magnesium dialkyls and Grignard reagents. G. H. Coleman and R. F. Blomquist (*J. Amer. Chem. Soc.*, 1941, **63**, 1692—1694).—NH_2Cl with $MgBu^aCl$, $MgBu^aBr$, and $MgBu^aI$, respectively, gives 43, 70, and 70% of NH_3 and 57, 29, and 12% of NH_2Bu^a. With $MgBu^a_2$ (prep. described) in Et_2O, Et_2O–dioxan, or dioxan at 0° it gives 0—14% of NH_3 and 82—96% of NH_2Bu^a. With an excess of $MgBu^a_2$ in dioxan it gives 97% of NH_2Bu^a. Addition of MgI_2 reduces the yield of NH_2Bu^a given by $MgBu^a_2$. If the $MgR_2 \rightleftharpoons MgRHal$ equilibrium is correctly determined by dioxan (the problem is discussed), $MgBu^a_2$ leads only to NH_2Bu^a, and $MgBu^aHal$ only to NH_3. R. S. C.

Grignard reaction involving the furan nucleus.—See A., 1942, II, 107.

IX.—PROTEINS.

Formation of fibres from non-fibrous native proteins. H. P. Lundgren (*J. Amer. Chem. Soc.*, 1941, **63**, 2854—2855).—Non-fibrous proteins [cryst. ovalbumin (**I**), hog thyroglobulin, wheat glutenin, casein, zein, and blood-albumin] are dissolved in dil., aq. detergent solutions and pptd. after a few min. by $(NH_4)_2SO_4$. The products can then be drawn into filaments but soon become tough. Details are given for (**I**) and an alkylarylsulphonate. R. S. C.

Conjugates synthesised from various proteins and the carbimides of aromatic polynuclear hydrocarbons. H. J. Creech and R. N. Jones (*J. Amer. Chem. Soc.*, 1941, **63**, 1670—1673).—Bovine serum-albumin undergoes conjugation with 3 : 4-benzpyrenyl-5- and 1 : 2-benzanthryl-10-carbimide to the same extent as horse serum-albumin. Very little conjugation occurs with horse serum ψ-globulin, bovine ψ-globulin, or ovalbumin before denaturation occurs. No conjugation occurs with zein. β-Anthrylcarbimide is conjugated with type III antipneumococcus rabbit serum, the product being strongly fluorescent. R. S. C.

Conjugation of horse serum-albumin with carbimides of polynuclear aromatic hydrocarbons. H. J. Creech and R. N. Jones (*J. Amer. Chem. Soc.*, 1941, **63**, 1661—1669).—When horse serum-albumin is coupled with polycyclic aromatic carbimides in aq. dioxan, the amount of carbimide combined increases with its solubility and with the concn. of dioxan. The products are purified by pptn. by $(NH_4)_2SO_4$ and $COMe_2$. The degree of coupling is determined by ultra-violet spectrophotometry. ~16 mols. of 1 : 2-benzanthracene-3- and -10- (**I**) and 10-methyl-1 : 2-benzanthracene-3-carbimide, 9 mols. of β-anthryl- and 1 : 2 : 5 : 6-dibenzanthryl-9-carbimide, and 4 mols. of 3 : 4-benzpyrenyl-5-carbimide (**II**) enter per mol. of protein under similar conditions, but in more conc. dioxan 30 mols. of (**I**) and 19 of (**II**) are combined. Properties of the products are recorded. R. S. C.

Threonine in maize. J. Giral and R. O. Cravioto (*Ciencia*, 1941, **2**, 104—206).—Hydrolysis of zein produces 5·80% of threonine (**I**) determined by the method of Block (A., 1939, II, 527). (**I**) with HNO_2 after removal of excess by $CO(NH_2)_2$ produces an intense wine-red colour with β-$C_{10}H_7$·OH in H_2SO_4. F. R. G.

Kinetics of formation of insoluble ovalbumin.—See A., 1942, I, 105.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Isolation of components of North Dakota lignite.—See A., 1942, I, 124.

Pongamia oil. Preparation and properties of pongamol. S. Rangaswami and T. R. Seshadri (*Indian J. Pharm.*, 1941, **3**, No. 1, *Reprint*).—Pongamol (A., 1940, II, 256), from EtOH extracts of old, or later EtOH extracts of fresh, pongamia oil, gives a red colour with $FeCl_3$, is 2·5—3 times as sol. in oils, and ⅓ as toxic (in 0·002% dil. aq. EtOH solution) to fish as karanjin, but is not toxic to earthworms in similar concns. A. Li.

New crystalline component of senna leaves (*Cassia angustifolia*). P. B. Murti and S. Rangaswami (*Indian J. Pharm.*, 1940, **4**, 203—205; cf. A., 1940, III, 273).—There is isolated a *compound*, $(C_{15}H_{18}O_9)_n$, m.p. 258° (decomp.) (sol. in cold aq. $NaHCO_3$; brown colour with $FeCl_3$). A. Li.

Bitter principles of neem oil. A. L. N. Murti, S. Rangaswami, and T. R. Seshadri (*Indian J. Pharm.*, 1940, **2**, No. 4-*Reprint*).—EtOH extraction of neem oil, the residual oil-cake, or the solid deposited by the oil on keeping, yields amorphous, bitter *substances*, $(C_5H_7O_2)_n$, slow decomp. from 115° (C_6H_6-sol.), and $(C_4H_7O_2)_n$, m.p. 72°, decomp. 110—115° (C_6H_6-insol.), which with boiling 7% H_2SO_4 give the characteristic odour of neem oil, but no sugar, and are not toxic to small fish or earthworms in 0·1% aq. EtOH solution. A. Li.

Hypericin, the photodynamic pigment from St. John's wort. N. Pace and G. Mackinney (*J. Amer. Chem. Soc.*, 1941, **63**, 2570—2574).—Pigments of *Hypericum perforatum* include chlorophyll, carotenoids, quercitin, hypericin (**I**), and a " residual red " pigment, the separation of which is described. Adsorption of (**I**) on $MgCO_3$–SiO_2 separates (**I**) into six compounds, mainly *hypericin*-X (25·3%), ? $C_{31}H_{28}O_9$, and -Y, $C_{29}H_{22}O_8$ (16·3%). The mol. wt. is determined by electrometric titration (glass electrode) in NaOH. Acetylation (Ac_2O–H_2SO_4) and quant. hydrolysis of the products discloses 6 OH in -*X* and -*Y* and absence of CO_2H. OMe and OEt are absent. Oxidation of crude (**I**) or -*Y* with Zn dust in H_2 at 450° gives an oil, b.p. 285°/758 mm. [mol. wt. (Rast) 330; blue fluorescence in light petroleum]. Absorption spectra of (**I**) and its hydrogenation product (-*X*; PtO_2-AcOH), and comparison with peniciliopsin, helianthrone, naphthadianthrone, etc., indicate that (**I**) may be a partly reduced polyhydroxyhelianthrone. The (**I**) is contained in black dots on the leaves and, when illuminated, gives a highly hæmolytic pigment. R. S. C.

Constituents of the volatile oil of catnip. I. Nepetalic acid, napatolactone, and related compounds. S. M. McElvain, R. D. Bright, and P. R. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 1558—1563).—*Nepeta cataria* (catnip) yields 0·3% of volatile oil, which contains nepetalic acid (**I**) (33%) (sol. in $NaHCO_3$), nepatolactone (**II**) (50%), and a neutral oil (14%), b.p. 210—214°/0·1 mm. Dissolution (exothermal) of (**II**) in aq. NaOH and careful acidification gives (**I**); thus extraction of the oil by aq. NaOH (85—90% sol.) gives much more (**I**). (**I**), m.p. 75—76°, b.p. 136—138°/0·1 mm., $[\alpha]$ +48·1°, is unstable when kept and is partly racemised during extraction. It is shown to be α-2- or -3-*carboxy*-x-*methyl*cyclo*pentylpropaldehyde* but to react also in the hydroxymethylene (*A*) and lactone form (*B*), $C_5H_7Me\langle^{CO-O}_{CHMe}\rangle CH\cdot OH$. When pure, it gives no CHI_3, but reduces Tollens' reagent and Fehling's solution. It gives a *semicarbazone*, m.p. 160—161°, and, with CH_2N_2, a *Me* ester (**III**), b.p. 113—115°/12 mm., $[\alpha]$ +16·1° (*semicarbazone*, m.p. 150—151°). With H_2SO_4 in boiling MeOH, (**I**) or (**III**) gives the *Me* ester *Me ether* (**IV**), b.p. 128—131°/12 mm., $[\alpha]_D^{25}$ +10·8° [from (*A*)], which does not react with semicarbazide but rapidly absorbs Br in CCl_4. H_2O_2–NaOH converts (**I**) or (**II**) into *nepetonic* [2- or 3-*acetyl*-y-*methyl*cyclo*pentane*-1-*carboxylic*] *acid* (**V**), b.p. 119—120°/0·2 mm., $[\alpha]$ −7·9° (*semicarbazone*, m.p. 168—169°), and HCO_2H. The Me ester, b.p. 64—66°/0·4 mm. (*semicarbazone*, m.p. 180—181°), of (**V**) is obtained by CH_2N_2 or from (**IV**) in EtOAc by O_3. I–KI–NaOH converts (**V**) into CHI_3 and *nepetic* [x-*methyl*cyclo*pentane*-cis-1 : 2- or -1 : 3-*dicarboxylic*] *acid* (81%), m.p. 117—118°, $[\alpha]$ −35·4° (*anhydride*, b.p. 98—99°/0·5 mm., $[\alpha]$ +22·8°), which shows 1 CMe. Acidification, without precautions, of a solution of (**I**) in aq. NaOH gives an oil, which, when distilled at 1 atm., gives (**II**), $C_5H_7Me\langle^{CO-O}_{CMe:CH}\rangle$, b.p. 71—72°/0·05 mm., $[\alpha]$ +3·6°, but (**II**) is obtained from the natural oil having $[\alpha]$ −13·0°. Aq. $Na_2Cr_2O_7$–H_2SO_4 oxidises (**I**) to *nepatalinic* [α-2- or -3-*carboxy*-x-*methyl*cyclo*pentylpropionic*] *acid*, m.p. 85—86°. Ac_2O at 100° converts (**I**), reacting as (*B*), into *nepatalic acid acetate*, $C_5H_5Me\langle^{CO-O}_{CHMe\cdot CH\cdot OAc}\rangle$, m.p. 68—69°, b.p. 124—126°/0·1 mm., $[\alpha]$ +72·2°. Unless otherwise stated, $[\alpha]$ are $[\alpha]_D^{23}$ in $CHCl_3$. R. S. C.

XI—ANALYSIS.

Signer method for determining mol. wts.—See A., 1942, I, 118.

Micro-method of chromatographic analysis.—See A., 1942, I, 112.

Micro-hydrogenation apparatus.—See A., 1942, I, 119.

Identification of nitriles. H. B. Cutter and M. Taras (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 830).—The nitrile RCN is reduced (Na–EtOH) to $CH_2R\cdot NH_2$, the EtOH evaporated from the acidified (HCl) solution, and the amine liberated (NaOH) and distilled into H_2O. PhNCS is added and on cooling the thiocarbamide $NHPh\cdot CS\cdot CH_2R$ is pptd., collected, washed with aq. EtOH, recrystallised, and identified by m.p. The following are described. *N-phenyl*-N′-iso*hexyl*-, m.p. 112°, -N′-*benzyl*-, m.p. 147°, -N′-p-*methylbenzyl*-, m.p. 144°, -N′-o-*methylbenzyl*-, m.p. 179°, and -N′-β-*naphthylmethyl*-*thiocarbamide*, m.p. 140°; αε-*bis*(*phenylthiocarbamido*)*pentane*, m.p. 148°, and αδ-*bis*(*phenylthiocarbamido*)*butane*, m.p. 168°. J. D. R.

Detection of coramine.—See A., 1942, III, 261.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

APRIL, 1942.

I.—ALIPHATIC.

Mechanism and kinetics of substitution at a saturated carbon atom.—See A., 1942, I, 148.

Production of saturated hydrocarbons.—See B., 1942, II, 2.

Dehydrogenation of paraffins and paraffin–olefine mixtures.—See B., 1942, II, 2.

Chemical reaction by the use of the thermal diffusion apparatus of Clusius and Dickel. I. Thermal polymerisation of methane. K. Hirota (*Bull. Chem. Soc. Japan*, 1941, **16**, 274—278).—The thermal polymerisation of CH_4 to higher hydrocarbons and H_2 is much more effective when carried out in a thermal diffusion column, 42% conversion and 87% of H_2 being obtained. F. J. G.

Effects of a high-voltage discharge on the thermal decomposition of ethane.—See A., 1942, I, 151.

Thermal behaviour of *n*-hexane.—See B., 1942, II, 1.

Action of sulphur on hydrocarbons under high pressure. W. Friedmann (*Refiner*, 1941, **20**, 395—406).—Experimental data obtained by autoclaving S with *n*-heptane, *iso*octane (**I**), or *iso*decane (**II**) at 280° are presented. The following general conclusions are reached. (1) The normal hydrocarbons change into branched systems, especially those which, under the directional influence of S, tend to form a five-membered ring with S in the bridge. (2) The branched hydrocarbons give simultaneously thiophanes and sulphides, *e.g.*, Me_2S. (3) Thiophanes react further with S forming (*a*) thiophens from normal paraffins, with partly dehydrogenated products as intermediates, (*b*) thiophthen (and probably thiophthanes) from normal paraffins, (*c*) polythiophanes or thiophane polysulphides from (**I**), and (*d*) dithienyls (probably hydrogenated dithienyls as an intermediate product) from (**II**). R. B. C.

Synthesis and properties of hydrocarbons of high mol. wt. J. N. Cosby and L. H. Sutherland (*Refiner*, 1941, **20**, 471—480).—Pure hydrocarbons of high mol. wt. are prepared, as a basis for establishing the chemical composition of lubricating oils. Pure intermediates are used, and the general procedure is the Grignard prep. of alcohols, followed by dehydration and hydrogenation, with careful purification at each stage by selective adsorption on SiO_2 gel or distillation. Purity is determined by time–temp. m.p. curve. In all cases, 85—95% of the final distillate has a const. val. for n, and vals. for η, d, heat of vaporisation, and dispersion are also given and their relation to constitution is discussed. The following are prepared: λ-, m.p. 0°, b.p. 180°/0·5 mm. (all b.p. recorded are at 0·5 mm.), ι-, m.p. 1·3°, b.p. 179°, η-, m.p. 3·2°, b.p. 180°, and ε-n-*butyldocosane*, m.p. 20·8°, b.p. 183°; η-n-*hexyl*-, m.p. 19·3°, b.p. 196°, and ι-n-*octyldocosane*, m.p. 8·6°, b.p. 209°; λ-n-*decyl*-, m.p. 8·7°, b.p. 215°, λ-α-*decahydronaphthyl*-, glass at −40°, b.p. 222°, λ-n-*amyl*-, m.p. −9·1°, b.p. 178°, λ-(γ-*amyl*)-, glass at −40°, b.p. 175°, λ-cyclo*hexyl*-, m.p. −7·2°, b.p. 197°, and λ-*phenyl-heneicosane*, m.p. 20·8°, b.p. 191°; λ-*phenyl*-Δ^{κ}-*heneicosene*, glass at −40°, b.p. 190°; ι-p-*tolyloctadecane*, glass at −40°, b.p. 173°; η-n-*hexyleicosane*, m.p. 10·2°, b.p. 181°; αα-*di*cyclo*hexyl*-, m.p. 37·6°, b.p. 193°, and αα-*diphenyl-tetradecane*, m.p. 17·9°, b.p. 194°; αα-*diphenyl*-Δ^{α}-*tetradecene*, m.p. 16·3°, b.p. 192°; ι-n-*octylheptadecane*, m.p. −13·8°, b.p. 172°; ι-n-*octyl*-Δ^{9}-*heptadecene*, glass at −40°, b.p. 181°; α-cyclo*hexyl*-γ-(β-cyclo*hexylethyl*)*hendecane*, glass at −40°, b.p. 195°; λ-n-decyldocosane, m.p. 1°, b.p. 222°/0·5 mm. A. T. P.

Activation energy of ionic substitution.—See A., 1942, I, 148.

Mechanism and kinetics of elimination reactions.—See A., 1942, I, 148.

Mechanism and kinetics of additions to olefinic compounds. G. Williams (*Trans. Faraday Soc.*, 1941, **37**, 749—763).—Addition of halogen to a double linking takes place most readily in strongly dissociating solvents, by an ionic mechanism; less readily in dissociating solvents such as AcOH by a mol. two-stage mechanism; and still less readily in non-dissociating solvents by catalytic mechanisms. Preliminary experiments are described in which the bromination of CH_2:CHBr at 300° is shown not to result in homogeneous addition; the effect of high temp. is to suppress surface addition and to promote substitution. F. L. U.

Reaction product of olefines with sulphuric acid.—See B., 1942, 11, 1.

Polymerisation of olefines induced by free radicals.—See A., 1942, I, 151.

Preparation of palladium and platinum synthetic high polymeride catalysts and relationship between particle size and rate of hydrogenation.—See A., 1942, I, 150.

Mercury-photosensitised reactions of ethylene.—See A., 1942, 1, 151.

Photochemistry of *iso*butene.—See A., 1942, I, 151.

Production of heptene [and other olefines].—See B., 1942, II, 2.

Olefines and diolefines from allylic chlorides. A. L. Henne, H. Chanan, and A. Turk (*J. Amer. Chem. Soc.*, 1941, **63**, 3474—3476).—With Mg in Et_2O, CH_2:CH·CHMeCl, b.p. 63°, CHMe:CH·CH_2Cl, b.p. 83°, or the crude mixture (*A*) thereof gives $(CHMe{:}CH{\cdot}CH_2)_2$ (b.p. 101·8°) 7, 4, or 3%, CHMe:CH·CH_2·CHMe·CH:CH_2 (**I**) (b.p. 111·0°) 57, 50, or 60%, and $(CH_2{\cdot}CH{:}CHMe)_2$ (**II**) (b.p. 124·5°) 3%, a little, or 4%, respectively. CH_2:CH·CH_2Cl and (*A*) (1 : 1) with Mg in Et_2O give CH_2:CH·$[CH_2]_2$·CH:CHMe (b.p. 93·7°) 34, (**I**) 21, $(CH_2{\cdot}CH{:}CH_2)_2$ (**III**) (b.p. 59·4°) 10, CH_2:CH·CHMe·CH_2·CH:CH_2 (b.p. 80°) 10, and (**II**) 1%. With MgBuCl in Et_2O, (*A*) gives CHMe:CH·C_5H_{11}-*n* (f.p. −94·04°, b.p. 125·2°) 85, CH_2:CH·CHMeBu$^{\alpha}$ 9, and (**I**) 6%. CH_2:CH·CH_2Cl with Mg gives (**III**) 60%, with CH_2:CHMe·CH_2Cl–Mg–Et_2O gives CH_2:CHMe·$[CH_2]_2$·CH:CH_2 (f.p. −128·88°, b.p. 88·1°) 47, $(CH_2{\cdot}CHMe{:}CH_2)_2$ (**IV**) (f.p. −75·6°, b.p. 114·3°) 30, and (**III**) 12%, with *n*-C_5H_{11}·MgCl gives Δ^{α}-*n*-octene (m.p. −102·11°, b.p. 121·6°) 80%, and with *iso*-C_5H_{11}·MgCl gives Bu$^{\beta}$·$[CH_2]_2$·CH:CH_2 (b.p. 113·19°) 60%. With Mg, CH_2:CHMe·CH_2Cl gives 65% of (**IV**), and with MgBuCl gives *n*-C_5H_{11}·CHMe:CH_2 (f.p. −90·1°, b.p. 119·3°) and some CMe_2:CHBu$^{\alpha}$. Piperylene hydrochloride and MgPrCl give only CHMe:CH·CHMePr$^{\alpha}$. Di*iso*crotyl hydrochloride and MgMeI give CHBu$^{\gamma}$:CHPr$^{\beta}$ (b.p. 114°) and CMe_2:CH·CHMePr$^{\beta}$ (b.p. 128·4°) (1 : 5). The following data are also recorded: CHMeEtPr$^{\alpha}$, b.p. 92·0°; CHMeEtBu$^{\alpha}$, f.p. −120·8°, b.p. 119·1°; $(CH_2Pr^{\beta})_2$, f.p. −91·49°, b.p. 109·3°; $CH_2Bu^{\beta}Bu^{\gamma}$, b.p. 123·0°; CHMePr$^{\beta}Bu^{\beta}$, b.p. 130·3°; n and d of all the compounds above. R. S. C.

Prolycopene, a naturally occurring stereoisomeride of lycopene. L. Zechmeister, A. L. Le Rosen, F. W. Went, and L. Pauling (*Proc. Nat. Acad. Sci.*, 1941, **27**, 468—474).—The pulp of the tangerine tomato was shaken with MeOH and light petroleum and the latter extract was chromatographed on $Ca(OH)_2$. The chromatogram showed about 15 layers which included lycopene (**I**), neolycopene, several other isomerides of (**I**), carotene and its isomerides, and a wide layer containing prolycopene (**II**), which when re-chromatographed yielded nine layers including (**I**). When observed spectroscopically, (**II**) is rapidly converted into (**I**) with I. The change (**II**) → (**I**) occurs more slowly in the presence of S or HBr in light petroleum. The stereochemical configuration of (**II**) is discussed. J. L. D.

Syntheses in the carotenoid series. II. New synthesis of squalene. J. Schmitt (*Annalen*, 1941, **547**, 115—122).—Geraniol is converted by PBr_3 and C_5H_5N in light petroleum into geranyl bromide, b.p. 105—110°/4 mm., which gives Et geranylacetoacetate, b.p. 152—158°/4 mm., hydrolysed by $Ba(OH)_2$ in aq. EtOH to geranylacetone [ζκ-dimethyl-$\Delta^{\epsilon\iota}$-undecadien-β-one], b.p. 130—133°/13 mm. This is transformed by Mg and $(CH_2{\cdot}CH_2Br)_2$ in Et_2O into squalene, b.p. 225—230°/1·5 mm. (hexachlorides, m.p. 114° and 143°; hexabromides, m.p. 116—118° and 136—138°) (cf. Heilbron *et al.*, A., 1926, 816; Karrer *et al.*, A., 1931, 333). Similarly, ψ-ionone, Mg, and $(CH_2{\cdot}CH_2Br)_2$ in Et_2O yield βζκοτω-*hexamethyl*-$\Delta\beta\zeta\kappa\mu\pi\sigma\phi\psi$-*tetracosaoctadiene*, a pale yellow liquid, b.p. 220—225°/1 mm., which gives intense colour reactions with conc. H_2SO_4 and with $SbCl_3$ but does not appear to give solid adducts with HCl or HBr. It appears to be dehydrogenated by *p*-O:C_6H_4:O at ~100° since a quinhydrone is formed. H. W.

Fluorinated derivatives of propane. IV. A. L. Henne and F. W. Haeckl (*J. Amer. Chem. Soc.*, 1941, **63**, 3476—3478).—The structure of $CHCl_2$·CClF·$CClF_2$ (**I**) is confirmed, but that of other products (A., 1939, II, 491) is corr. Gradually distilling CCl_3·CClF·$CClF_2$ (**I**) with SbF_3 (0·5) + Cl_2 (0·05 mol.) gives αaβγ-*tetrachloro*-αβγγ-*tetrafluoropropane* (70%), m.p. −58°, b.p. 112·5—112·6°, also obtained

from (I) by successive fluorination (to $CHClF{\cdot}CClF{\cdot}CClF_2$, b.p. 90°) and chlorination. $CCl_2{:}CF{\cdot}CCl_3$ (prep. from $CHCl_2{\cdot}CClF{\cdot}CCl_3$ by NaOH–EtOH) with SbF_3 (1·5 mols.) at 125° gives $CCl_2{:}CF{\cdot}CF_3$ (0·37 mol.) [with $CCl_2{:}CF{\cdot}CClF_2$ (0·27 mol.)], which with Cl_2 in light gives *aaaβ-tetrachloro-βγγγ-tetrafluoropropane*, m.p. 12·1°, b.p. 112·4—112·6°. The following corrections (cf. *loc. cit.*) are made: *aaγ*-trichloro-*βγγγ*- becomes *αβγ-trichloro-αβγγ-tetrafluoropropane*; *aaaβ*-tetrachloro-*βγγγ*- becomes *aaβγ-tetrachloro-αβγγ-tetrafluoropropane*; *aa*-dichloro-*βγγγ*- becomes ? *aγ-dichloro-αβγγ-tetrafluoro-Δ^a-propene*; *aa*-dichloro-*αβ*-dibromo-*βγγγ*- becomes *aγ-dichloro-αβ-dibromo-αβγγ-tetrafluoropropane*. R. S. C.

Synthesis of organic *aaa*-trifluorides. A. L. Henne, A. M. Whaley, and J. K. Stevenson (*J. Amer. Chem. Soc.*, 1941, **63**, 3478—3479).—Replacement of Cl by F occurs rapidly when compounds containing $C{\cdot}C{\cdot}CCl_3$ are heated with SbF_3 (1·5 mols.). $CCl_2{:}CCl{\cdot}CCl_3$ and SbF_3 at 125—140° give *aaβ-trichloro-γγγ-trifluoro-* (I) (43%), f.p. −114·7°, b.p. 88·3°, *aaβγ-tetrachloro-γγ-difluoro-* (28%), f.p. −103·0°, b.p. 128·0°, and *aaβγγ-pentachloro-γ-fluoro-Δ^a-propene* (13%), b.p. 170·2°. *βγ-Dichloro-aaγγ-tetrafluoro-Δ^a-propene* [prep. from $CCl_2(CClF_2)_2$ by Zn–EtOH], f.p. −121·2°, b.p. 44·7°, and SbF_3 give *β-chloro-aaγγγ-pentafluoro-Δ^a-propene* (47%), f.p. −130·4°, b.p. 6·8°, converted by Cl_2 into *aaβ-trichloro-αβγγγ-pentafluoropropane* (II), f.p. −4·30°, b.p. 72·0°. Cl_2 and (I) give *aaaββ-pentachloro-γγγ-trifluoropropane* (III), f.p. 109·1°, b.p. 153·1°, also obtained from $CEtCl_3$ by way of $CEtF_3$. With SbF_3, $CPhCl_3$ gives $CPhF_3$ (60%; much decomp.), $CHCl{:}CCl{\cdot}CCl_3$ gives *aβ-dichloro-γγγ-trifluoro-Δ^a-propene*, f.p. −109·23°, b.p. 53·7°, $CCl_2{:}CF{\cdot}CCl_3$ gives $CCl_2{:}CF{\cdot}CF_3$, b.p. 46·0° (and thence *aaaβ-tetrachloro-βγγγ-tetrafluoropropane*, m.p. 12·1°, b.p. 112·4°), and $CCl_2{:}CH{\cdot}CCl_3$ gives $CCl_2{:}CH{\cdot}CF_3$. $CEtF_3$ gives (III) and thence (II). R. S. C.

Catalytic conversion of olefines into alcohols.—See B., 1942, II, 3.

Reactions of (+)- and (−)-γ-methyl-α-ethylallyl alcohol and their derivatives. R. S. Airs, M. P. Balfe, and J. Kenyon (*J.C.S.*, 1942, 18—26).—dl-*γ-Methyl-α-ethylallyl H phthalate*, m.p. 52—53°, is resolved via the brucine salt, m.p. 168°, into the (+)- and (−)-*form* (I), m.p. 70·5°, $[\alpha]_{5461}$ ±15° in $CHCl_3$, hydrolysed by 5N-NaOH (more dil. NaOH causes racemisation) to the (+)- (II) and (−)-*alcohol* (III), $[\alpha]_{5461}$ ±14·24° in CS_2. On reduction (H_2, PtO_2), (II) yields (+)-, b.p. 131—133°, $[\alpha]^{20}_{5893}$ +7·09° (homogeneous) (H phthalate, m.p. 48—49°, $[\alpha]^{20}_{5893}$ +9·70° in $CHCl_3$), and the freshly prepared *dl*-alcohol (IV) yields *dl*-$CHEtPr^a{\cdot}OH$, b.p. 132·5—133·5° (H phthalate, m.p. 75—76°); a 2-years-old specimen (V) gives a hexanol, b.p. 131—133°. (IV) gives a p-*xenylurethane*, m.p. 102°, and (V) a mixture of this (75%) with the *p*-xenylurethane, m.p. 84—86°, of $CHEt{:}CH{\cdot}CHMe{\cdot}OH$ (VI). dl-*γ-Methyl-α-ethylallyl chloride* ($SOCl_2$), b.p. 123—124° (slight decomp.), is hydrolysed (H_2O, $CaCO_3$) to a mixture of (IV) and (VI), reduced to *dl*-$CHEtPr{\cdot}OH$ (p-*xenylurethane*, m.p. 132—133°) and *dl*-$CHMeBu{\cdot}OH$ (p-*xenylurethane*, m.p. 91—92°; *H. phthalate*, m.p. 48°). (−)-γ-Methyl-α-ethylallyl chloride [from (II)], a^{19}_{5461} −14·75°, is hydrolysed to a hexenol, a^{20}_{5461} −0·07°, reduced to a hexanol, b.p. 132—137°, a^{20}_{5461} +0·02° (H phthalate, $[\alpha]_{5461}$ +0·07° in $CHCl_3$). (II) and (III) undergo mutarotation at varying rates, increased by a trace of acid. The ratio of $[\alpha]$ to that of the H phthalate shows that (V) has undergone 27% racemisation, and contains 41% of (+)-$CHMe{:}CH{\cdot}CHEt{\cdot}OH$ and 32% of (+)-$CHEt{:}CH{\cdot}CHMe{\cdot}OH$. It is suggested that this rearrangement is due to a pseudo-cyclic structure of the allylic alcohols, confirmed by parachor vals. of 12 derivatives, including dl-*γ-methyl-α-ethylallyl acetate*, b.p. 54—56°, and *benzoate*, b.p. 144—145°. The p-*nitrobenzoate* has m.p. 35—37°. (I) with boiling MeOH yields *Me γ-methyl-α-ethylallyl ether*, b.p. 110—112°, a^{21}_{5461} −0·18°, also obtained, a^{23}_{5461} + 6·88°, from the alcohol prepared from the same specimen of (I), with K, then MeI. A. Li.

Catalytic dehydrogenation and condensation of aliphatic alcohols. II. V. I. Komarewsky and J. R. Coley (*J. Amer. Chem. Soc.*, 1941, **63**, 3269—3270).—Conversion of alcohols into ketones by Cr_2O_3 at, usually, 400—425° (cf. A., 1941, II, 158) is extended to *n*-C_{3-8}, *n*-C_{10}, and *n*-C_{18} alcohols, yields being 27·8—83·2%. EtOH + *n*-$C_8H_{17}{\cdot}OH$ and *n*-$C_5H_{11}{\cdot}OH$ + *n*-$C_{10}H_{21}{\cdot}OH$ give *n*-$C_7H_{15}{\cdot}COMe$ (41·7%) and *n*-$C_9H_{19}{\cdot}COBu^a$ (27·2%), respectively, with smaller amounts of *sym.* ketones, except $COMe_2$ which is never obtained. Aldehydes give similarly better, and aldols still better, yields, confirming the mechanism previously proposed (*loc. cit.*). At 760 and 125—135 mm., *n*-$C_8H_{17}{\cdot}OH$ gives 56 and 73·9%, respectively, of ketone. The following are new: aldol-2 : 4-dinitrophenylhydrazone, m.p. 125·5—126·5°; $CO(C_6H_{13}\text{-}n)_2$, m.p. 39—40°; n-*tetradecan-ε-ol*, m.p. 28·5°, and *-one*, m.p. 25·5—26°; n-*nonadecan-κ-ol*, m.p. 65·5°. R. S. C.

Denatured alcohol containing 1 : 3-dioxolan.—See B., 1942, II, 3.

Separation of *iso*- and *n*-butyl alcohols from hydrocarbons by azeotropic distillation. R. Negishi and C. Isobe (*Bull. Chem. Soc. Japan*, 1941, **16**, 278—284).—Bu^aOH and $Bu^\beta OH$ may be separated from hydrocarbons (PhMe or gasoline) by extraction with H_2O followed by distillation of the azeotropic mixture. F. J. G.

Mechanism and kinetics of anionotropic change.—See A., 1942, I, 148.

Structure–property relations of isomeric octanols. G. L. Dorough, H. B. Glass, T. L. Gresham, G. B. Malone, and E. E. Reid (*J. Amer. Chem. Soc.*, 1941, **63**, 3100—3110).—Relations are tabulated between structure of the carefully purified 4 octanols and 18 methylheptanols and their b.p. at 20, 100, 300, and 760 mm., the difference between the b.p. and that of the hydrocarbon, latent heat of vaporisation, d^0_4, d^{25}_4, the difference between *d* and that of the hydrocarbon, expansion (0—25° and 80—100°), n^{25}_D, m.p., molal heat capacity, solubility in H_2O, η, total surface energy, parachor, Ramsey and Shields const., dielectric const., fluidity, association at 15°, *X*-ray secondary peak, rate of esterification with AcOH at 136±0·5° (1 and 100—200 hr.) and Ac_2O at 35±0·01° (125 hr.), oxidation by O_2 at 137° (rate and ratio CO_2/CO produced), and toxicity to *Lupinus albus*, goldfish, newts, and tadpoles. Data include the following; those in parentheses refer to α-naphthylurethanes and 3 : 5-dinitrobenzoates, respectively. *n*-Octan-α-, m.p. −15·0°, b.p. 195·0° (m.p. 67·0°, 60·8°), -β-, m.p. −31·6°, b.p. 180·0° (an oil; m.p. 32·3°), -γ-, m.p. −45·0°, b.p. 173·0° (m.p. 54·0°, 69·4°), and -δ-ol, m.p. −40·7°, b.p. 176·3° (m.p. 65·5°, 53·9°). ζ-Methyl-*n*-heptan-α-, m.p. (of glass) −106·0°, b.p. 187·6° (m.p. 68·5°, 58·3°), -β-, m.p. (of glass) −105·0°, b.p. 171·8° (an oil; m.p. 34·4°), and -γ-ol, m.p. −58·5°, b.p. 158·5° (oils). *β-Methyl*-n-*heptan-α-* (from *n*-$C_5H_{11}{\cdot}CHMe{\cdot}MgBr$ and CH_2O), m.p. −112·0°, b.p. 175·4° (an oil; m.p. 50·6°), -β-, m.p. −50·4°, b.p. 156·1° (m.p. 57·5°; an oil), -γ-, m.p. (of glass) −85·0°, b.p. 167·2° (m.p. 73·0°, 38·5°), and -δ-ol, m.p. (of glass) −81·0°, b.p. 166·3° (m.p. 70·0°, 71·7°). ε-*Methyl*-n-*heptan-α-* {from $CHMeEt{\cdot}[CH_2]_2{\cdot}MgBr$ (I) and $[CH_2]_2O$}, m.p. (of glass) −104·0°, b.p. 186·5° (oils), -β- [from (I) and MeCHO], m.p. (of glass) −120·0°, b.p. 171·9° (oils), and -γ-ol, m.p. 91·2°, b.p. 153·4° (an oil; m.p. 89·8°). γ-Methyl-*n*-heptan-α-, m.p. −90·0°, b.p. 185·8° (oils), -β- (from $CHMeBu^a{\cdot}MgBr$ and MeCHO), m.p. (of glass) −114·0°, b.p. 166·1° (oils), -γ-, m.p. (of glass) −83·0°, b.p. 159·4° (m.p. 52·0°; an oil), and -δ-*ol* (from $CHMeEt{\cdot}MgBr$ and Pr^aCHO), b.p. 164·7° (an oil; m.p. 91·8°). δ-*Methyl*-n-*heptan-α-* (from $CHMePr^a{\cdot}CH_2{\cdot}MgBr$ and $[CH_2]_2O$), b.p. 182·7° (oils), -β-, m.p. (of glass) −102·0°, b.p. 171·7° (oils), -γ-, m.p. (of glass) −123·0°, b.p. 155·4° (an oil; m.p. 92·4°), and -δ-ol, m.p. (of glass) −82·0°, b.p. 160·8° (m.p. 90·0°; an oil). *n*-$C_5H_{11}{\cdot}OH$, b.p. 137·8°. $CHMePr^a{\cdot}OH$, b.p. 119·5°. $CH_2Bu^\beta{\cdot}OH$, b.p. 130·5°. $CHMeEt{\cdot}CH_2{\cdot}OH$, b.p. 128·0°/752 mm. $Bu^\beta{\cdot}[CH_2]_2{\cdot}OH$, b.p. 151·7°/758 mm. $CHMePr^a{\cdot}CH_2{\cdot}OH$, b.p. 148·9°/760 mm. $CHMeBu^a{\cdot}OH$, b.p. 139·7°/759 mm. *n*-$C_5H_{11}{\cdot}CHMe{\cdot}OH$, b.p. 158·5°/754 mm. $CHMePr^a{\cdot}[CH_2]_2{\cdot}OH$, b.p. 94·6°/40 mm. *n*-$C_5H_{11}Br$, b.p. 127·8°/745 mm. Bu^aBr, b.p. 101·3°. $Bu^\beta{\cdot}[CH_2]_2{\cdot}Br$, b.p. 147·6°. $CHMeEt{\cdot}CH_2Br$, b.p. 121·0°. $Bu^\beta Br$, b.p. 91·2°. *n*-$C_5H_{11}{\cdot}CHMeBr$, b.p. 81·7°/45 mm. $CHMeEt{\cdot}[CH_2]_2{\cdot}Br$, b.p. 146·5°. $CH_2Bu^\beta Br$, b.p. 117·5°. $CHMeEtBr$, b.p. 91·2°/750 mm. $CHMePr^aBr$, b.p. 118·4°. $CHMePr^a{\cdot}[CH_2]_2{\cdot}Br$, b.p. 87·5°/50 mm. EtCHO, b.p. 48·8°. $CHMeBu^aBr$, b.p. 143·9°/750 mm. $CHMePr^a{\cdot}CH_2Br$, b.p. 83·8°/100 mm. Pr^aCHO, b.p. 74·9°. $Pr^\beta CHO$, b.p. 63·5°. COMeEt, b.p. 80·6°. M.p. are corr. R. S. C.

β-Methyltetradecan-α-ol. K. Lindblad and E. Stenhagen (*J. Amer. Chem. Soc.*, 1941, **63**, 3539—3540).—*n*-$C_{12}H_{25}{\cdot}CHMe{\cdot}CO_2Et$, Na, BuOH, and (later) EtOH in light petroleum give *β-methyl-n-tetradecan-α-ol* (40%), m.p. 32·0—32·2°, b.p. 134°/2 mm. R. S. C.

Amyl nitrite. Determination and decomposition.—See B., 1942, II, 1.

Explosion hazard in the chlorination of alkyl*iso*thiocarbamides to prepare alkanesulphonyl chlorides. K. Folkers, A. Russell, and R. W. Bost (*J. Amer. Chem. Soc.*, 1941, **63**, 3530—3532).—During the prep. of $AlkSO_2Cl$ from aq. $SAlk{\cdot}C(:NH){\cdot}NH_2{,}HCl$ by Cl_2, a violent explosion may occur if an excess of Cl_2 is used. NCl_3 is probably formed. R. S. C.

Condensation of sulphoxides with *p*-toluenesulphonamide and substituted acetamides. D. S. Tarbell and C. Weaver (*J. Amer. Chem. Soc.*, 1941, **63**, 2939—2942).—Condensation of *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$ (I) with R_2SO in Ac_2O at 100° or boiling P_2O_5–$CHCl_3$ gives sulphilimines, $R_2S{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me\text{-}p$, the structure of which is proved by prep. also from R_2S and chloramine-*T* (Mann *et al.*, *J.C.S.*, 1922, **121**, 1052; Clarke *et al.*, A., 1927, 243). The products are unaffected by alkali, dissolve in cold HCl (? salt-formation), and in hot HCl are hydrolysed to R_2SO and (I). Sulphilimines, $R_2S{\rightarrow}NR'$, are similarly obtained by Ac_2O in which $R' = CCl_3{\cdot}CO$ or $CHCl_2{\cdot}CO$, but not if $R' = CH_2Cl{\cdot}CO$ or Bz. Analogous reactions are discussed. Prep. of $[CH_2]_4{>}S$, b.p. 119—120°, from $Br{\cdot}[CH_2]_4{\cdot}Br$ and Na_2S in aq. EtOH is modified to give 64% yield. *Tetramethylene sulphoxide* (II), b.p. 105—107°/12 mm., is obtained by 30% H_2O_2 at 0° or in $COMe_2$. The following are described: Et_2, 83—85°/12 mm., Me_2, b.p. 85—87°/25 mm., and Ph_2 sulphoxide, b.p. 85—87°/25 mm.; $[CH_2]_4{>}SO_2$, m.p. 10—10·5°; diethyl-, m.p. 145—146°, *tetramethylene-*, m.p. 134—135°, and *diphenyl-* (prep. by P_2O_5 but not Ac_2O), m.p. 108—110°, *-sulphin*-p-*toluenesulphonylimine*; $CCl_3{\cdot}CO{\cdot}NH_2$ (prep. by boiling $CCl_3{\cdot}CO_2H$ with $SOCl_2$ and a little C_5H_5N in Et_2O and later treatment with NH_3), m.p. 139—141°;

tetramethylenesulphintrichloroacetylimine, m.p. 116—117°; *tetramethylene-*, m.p. 149—151°, and *diethyl-sulphindichloroacetylimine*, m.p. 112—113°. The following condensations failed: (OH·[CH_2]$_2$)$_2$SO–(I); Et_2SO– or Ph_2SO–CCl_3·CO·NH_2; Et_2SO– or (III)–NH_2Bz–Ac_2O (gives PhCN); fluorene–Me_2SO or –(II); 2 : 7-dinitrofluorene–Me_2SO or –(II). Sulphoxides do not show "CO" properties; *e.g.*, (II) does not react with CH_2N_2 or PhCHO. R. S. C.

Configuration of naturally occurring glycerol esters. H. O. L. Fischer and E. Baer (*Schweiz. med. Wschr.*, 1941, **71**, 321—322).—The Na compounds of *d*(+)- and *l*(−)-*iso*propylideneglycerol with s-$C_{18}H_{33}I$ and $C_{18}H_{27}I$ in boiling $(CH_2{\cdot}OMe)_2$ yielded the :CMe_2 compounds of α-hexadecyl- and α-octadecyl-glycerol; hydrolysis with AcOH gave the free alcohols, identical with chimyl alcohol (I), m.p. 62—63°, and batyl alcohol (II), m.p. 71°. The two enantiomorphic forms of synthetic (II) have [α] ±0°. The diacetylated synthetic batyl alcohols had $[\alpha]_{6461}^{20}$ ±8·6° in $CHCl_3$ (c = 11·2). A crude prep. of the glyceryl ethers from the unsaponifiable fraction of *Chimaera monstrosa* liver oil was treated with $COMe_2$, giving a product with $[\alpha]_D$ −14·0° (in substance); the two :CMe_2 compounds of the synthetic (II) had $[\alpha]_D^{40}$ ±12·6° in melted substance. (II) belongs to the *d*-series, so does selachyl alcohol, as it can be transformed into *d*-batyl alcohol by catalytic reduction. Natural (I) is dextrorotatory. A. S.

Preparation of alkane-αω-disulphonic acids. S. Zuffanti and R. Hendrickson (*J. Amer. Chem. Soc.*, 1941, **63**, 2999—3000).—Ethane-αβ-, m.p. 97°, *propane-*αγ-, b.p. 157°/1·4 mm., n-*butane-*αδ-, m.p. 84°, n-*pentane-*αε-, b.p. 198°/1·7 mm., n-*hexane-*αζ-, m.p. 78°, and n-*decane-*ακ-, m.p. 76°, *-disulphonic acid* are obtained by treating the Na_2 salts in MeOH with dry HCl and give m-$C_6H_4Me{\cdot}NH_2$ salts, m.p. 230°, 222°, 214°, 187°, 158°, and 178°, respectively. R. S. C.

Mechanism and kinetics of carboxylic ester hydrolysis and carboxyl esterification.—See A., 1942, I, 148.

Catalytic reduction of esters using nickel alone as a catalyst. C. L. Palfray. **Behaviour of esters over Raney nickel.** P. L. de Benneville, W. R. McClellan, and R. Connor (*J. Amer. Chem. Soc.*, 1941, **63**, 3540—3541, 3541—3542).—Concerning priority. R. S. C.

Identification of organic acids by use of *p*-bromobenzyl-ψ-thiuronium bromide. B. T. Dewey and H. G. Shasky (*J. Amer. Chem. Soc.*, 1941, **63**, 3526—3527).—p-*Bromobenzyl-ψ-thiuronium bromide* [prep. from *p*-$C_6H_4Br{\cdot}CH_2Br$ and $CS(NH_2)_2$ in hot EtOH], m.p. 213°, with the Na or K salt of the acid in hot EtOH gives the *formate*, m.p. 148°, *acetate*, m.p. 149°, *propionate*, m.p. 146°, *butyrate*, m.p. 142°, n-, m.p. 146°, and iso-*valerate*, m.p. 148°, *hexoate*, m.p. 146°, *heptoate*, m.p. 147°, *octoate*, m.p. 145°, α-*ethyl*-n-*butyrate*, m.p. 141°, *dodecoate*, m.p. 142°, *palmitate*, m.p. 135°, *stearate*, m.p. 135°, *oxalate*, m.p. 194°, *malonate*, m.p. 139°, *succinate*, m.p. 167°, *glutarate*, m.p. 149°, *chloroacetate*, m.p. 154°, *trichloroacetate*, m.p. 146°, *oleate*, m.p. 133°, *benzoate*, m.p. 154°, o-, m.p. 163°, m-, m.p. 154°, and p-*bromo-*, m.p. 173°, o-, m.p. 168°, m-, m.p. 150°, and p-*chloro-*, m.p. 163°, o-, m.p. 154°, m-, m.p. 152°, and p-*iodo-benzoate*, m.p. 181°, *cinnamate*, m.p. 170°, *phthalate*, m.p. 166°, *salicylate*, m.p. 168°, o-, m.p. 151°, m-, m.p. 151°, and p-*toluate*, m.p. 165°. The salts are anhyd. and fairly stable. Depression of the m.p. on admixture is 6—12°. M.p. are corr. R. S. C.

Preparation and properties of acetic acid-d_1. H. Linschitz, M. E. Hobbs, and P. M. Gross (*J. Amer. Chem. Soc.*, 1941, **63**, 3234).—Ac_2O and 99·6% D_2O give AcOD (~99% pure), m.p. 15·66±0·05°, d_4^{20} 1·0527, d_4^{25} 1·0588, n_D^{20} 1·37102. R. S. C.

Alcoholysis of polyvinyl acetate.—See A., 1942, I, 150.

Chlorination of propyl trichloroacetates. C. W. Gayler and H. M. Waddle (*J. Amer. Chem. Soc.*, 1941, **63**, 3358—3359).—Contrary to Maxwell (*Thesis*, 1933), $CCl_3{\cdot}CO_2Pr^n$ (1), b.p. 69°/10 mm., and Cl_2 (1 mol.) in light at 120° give β- (0·30 mol.), b.p. 94°/8 mm., γ- (0·28 mol.), b.p. 107°/8 mm., and (? α)-*chloro*-n-*propyl trichloroacetate* (0·02 mol.) [hydrolysed to HCl and a substance (2 : 4-dinitrophenylhydrazone, m.p. 162°)]. $CCl_3{\cdot}CO_2Pr^\beta$, b.p. 65°/10 mm., gives similarly CMe_2Cl (0·25 mol.), b.p. 72°/8 mm. (with cold aq. KOH rapidly gives $COMe_2$), and $CH_2Cl{\cdot}CHMe$ *trichloroacetate* (0·31 mol.), b.p. 93·5°/8 mm. [hydrolysed by hot (not cold) 25% KOH to $(CH_2{\cdot}OH)_2$]. Cl·[CH_2]$_3$·OH, b.p. 165° (α-naphthylurethane, m.p. 76·5°), is described. R. S. C.

Dimethylneopentylacetic [ααγγ-tetramethyl-*n*-valeric] acid, its methyl ester, amide, and anilide. F. C. Whitmore, W. R. Wheeler, J. D. Surmatis (*J. Amer. Chem. Soc.*, 1941, **63**, 3237).—Addition of diisobutylene hydrochloride and EtBr–Et_2O to Mg–MgEtBr–Et_2O and subsequent treatment with CO_2 gives 34% of $CH_2Bu^\gamma{\cdot}CMe_2{\cdot}CO_2H$, m.p. 45°, b.p. 229·6°/732 mm. (Me ester, b.p. 176·2°/732 mm.; amide, m.p. 71°; *anilide*, m.p. 78°) (cf. A., 1941, II, 345). R. S. C.

Optically active αβ-diglycerides. J. C. Sowden and H. O. L. Fischer (*J. Amer. Chem. Soc.*, 1941, **63**, 3244—3248).—*d*(+)-*iso*-Propylideneglycerol in boiling Et_2O with, first, Na and then CH_2PhBr or, better, in $(CH_2{\cdot}OMe)_2$ with $NaC_{10}H_7$ and then CH_2PhBr gives d(+)-iso*propylideneglycerol α'-CH$_2$Ph ether* (I), b.p. 95—97°/0·3 mm., $[\alpha]_D$ +16·8°. The corresponding α'-Me ether, b.p. 45—47°/10 mm., $[\alpha]_D$ +22·5°, is similarly prepared. In boiling N-H_2SO_4, (I) gives l-*glyceryl α-CH$_2$Ph ether* (II), b.p. 138—139°/0·3 mm., $[\alpha]_D$ +5·3°, but in boiling 90% AcOH gives another product. With RCOCl in $CHCl_3$–quinoline at 37°, (II) gives d-*glyceryl α-CH$_2$Ph ether α'β-distearate* (III), m.p. 50·5—51°, $[\alpha]_D$ +6·1° in $CHCl_3$, and *-dipalmitate*, m.p. 42—42·5°, $[\alpha]_D$ +6·3° in $CHCl_3$; the *α'β-dibutyrate*, b.p. 140° (bath)/0·005 mm., $[\alpha]_D$ +15·5°, is obtained in C_5H_5N at 0°. With MeI, $CaSO_4$, and Ag_2O, (II) gives d-*glyceryl α-CH$_2$Ph α'β-Me$_2$ ether* (IV), b.p. 147—148°/13 mm., $[\alpha]_D$ +4·1°. Hydrogenation (PtO_2; slightly >1 atm.) of (III) in AcOH gives d-*αβ-distearin*, m.p. 74·5—75°, $[\alpha]_D$ −2·7° in $CHCl_3$ (*acetate*, m.p. 56·5—57°, $[\alpha]_D$ ±0° in $CHCl_3$), the p-*nitrobenzoate*, m.p. 67—67·5°, $[\alpha]_D$ −1·4° (−1·3°) in $CHCl_3$, of which is obtained therefrom by *p*-$NO_2{\cdot}C_6H_4{\cdot}COCl$ in C_5H_5N and from *l*-glyceryl α-*p*-nitrobenzoate by stearyl chloride in quinoline at room temp. d-*αβ-Dipalmitin*, m.p. 67—67·5°, $[\alpha]_D$ −2·3° in $CHCl_3$ [p-*nitrobenzoate*, m.p. 60—60·5°, $[\alpha]_D$ −1·6° (−1·4°) in $CHCl_3$], and d-*αβ-dibutyrin*, b.p. 95° (bath)/0·001 mm., $[\alpha]_D$ +0·69° (homogeneous), ±0° in $CHCl_3$, +1·7° in C_5H_5N, are similarly obtained, but (IV) gives d-*glyceryl* α-cyclo*hexylmethyl α'β-Me$_2$ ether*, b.p. 135—138°/14 mm., $[\alpha]_D$ +4·9°. R. S. C.

Isomerisation of polyene acids and carotenoids. Preparation of β-elæostearic and β-licanic acid. H. H. Strain (*J. Amer. Chem. Soc.*, 1941, **63**, 3448—3452).—The isomerisation of oleic acid (I) and the readier isomerisation of α-elæostearic acid (II) and its esters by various reagents are described. That of (I) by $NaNO_2$–30% HNO_3 and of (II) or α-licanic acid by a little I in MeOH has preparative val. Dihydroxyxanthophylls are converted by I into more strongly, and then (more I, longer reaction) into less strongly, adsorbed pigments. Absence of OH decreases the ease of isomerisation. Esterification of OH also decreases the ease of change and leads to products which are separable by chromatography only after hydrolysis. Some adsorbents, *e.g.*, synthetic, activated Mg silicate, although neutral in H_2O, change carotenoids into blue substances similar to those obtained by strong acids or very strong bases. Care is thus needed in isolation of naturally occurring pigments, as accompanying acids may cause isomerisation; this may be avoided by adding org. bases, *e.g.*, $NPhMe_2$, C_5H_5N. R. S. C.

Electrolytic preparation of ethyl glyoxylate. W. Oroshnik and P. E. Spoerri (*J. Amer. Chem. Soc.*, 1941, **63**, 3338—3339).—Electrolytic reduction of $Et_2C_2O_4$ at, best, Pd–Hg (53% yield) or Hg (50%) cathodes gives OEt·CH(OH)·CO_2Et, converted by P_2O_5 into CHO·CO_2Et. R. S. C.

Condensations. XVI. Acylations and alkylations of sodium enolates of aliphatic esters. Syntheses of αα-disubstituted β-keto-esters and other compounds. B. E. Hudson, jun., and C. R. Hauser (*J. Amer. Chem. Soc.*, 1941, **63**, 3156—3162; cf. A., 1941, II, 130).—Prep. (large scale) of CPh_3Cl and $NaCPh_3$ is described. For condensations using $NaCPh_3$ it is best to allow it to react completely (disappearance of red colour) or nearly so with the "enolising" compound in, *e.g.*, Et_2O before adding the second reagent. Reactions described below are thus effected. $Bu^\beta CO_2Et$ gives $Bu^\beta CO{\cdot}CHPr^\beta{\cdot}CO_2Et$ (63%). $Bu^\gamma CO_2Et$ with $Pr^\alpha CO_2Et$ or $Pr^\beta CO_2Et$ gives mixed β-CO-esters owing to the formation (and later condensation) of enolates of the latter esters. $Pr^\beta CO_2Et$ with $Et_2C_2O_4$ gives 61% of $CO_2Et{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et$, but with HCO_2Et gives only 16% of $HCO{\cdot}CMe_2{\cdot}CO_2Et$. CHRR'·$CO_2$Et with R''COCl gives 51—74% of R''CO·CRR'·CO_2Et, examples being (*a*) R = R' = Me, R'' = Me, Pr^α, Pr^β, and Ph, (*b*) R = Me, R' = Et, R'' = Et, Bu^β, and Ph, and (*c*) R' = R = Et, R'' = Ph. *Et αα-dimethyl-acetoacetate semicarbazone*, m.p. 119°, and *Et β-keto-αδ-dimethyl-α-ethyl*-n-*hexoate*, b.p. 116—119°/15 mm., are described. $Pr^\beta CO_2Et$ and $ClCO_2Et$ give 75% of $CMe_2(CO_2Me)_2$. Interaction of EtOAc with RCOCl gives mainly $(RCO)_2CH{\cdot}CO_2Et$: thus, with $Pr^\alpha COCl$ it gives 49% of $(Pr^\alpha CO)_2CH{\cdot}CO_2Et$; addition of $CH_2Na{\cdot}CO_2Et$ to EtCOCl (excess) in Et_2O at 0° gives *Et β-keto-β*-n-*propionyl*-n-*valerate* (39%), b.p. 98—102°/9 mm., and $EtCO{\cdot}CH_2{\cdot}CO_2Et$ (15%); $CHPr^\beta Na{\cdot}CO_2Et$ and $ClCO_2Et$ give *Et β-carbethoxy-β-methylglutarate* (29%), b.p. 150—152°/15 mm., and $CHPr^\beta(CO_2Et)_2$ (13%). $Pr^\beta CO_2Et$ with PhNCO gives $CO_2Et{\cdot}CMe_2{\cdot}CO{\cdot}NHPh$ (33%) (best method of prep.). Alkylation of EtOAc is impossible owing to condensation, but $Bu^\beta CO_2Et$ and $PhSO_2Et$ give $CHEtPr^\beta{\cdot}CO_2Et$ (33%), and $Pr^\beta CO_2Et$ and $CMe_2Br{\cdot}CO_2Et$ give $(CMe_2{\cdot}CO_2Et)_2$ (30%), also obtained (26%) from the enolate by I. $Pr^\beta CO_2Et$ with $(CH_2)_2O$ gives αα-dimethyl-γ-butyrolactone (55%), b.p. 195·5—197·5°. R. S. C.

Introduction of substituted vinyl groups. VIII. Acetoacetic ester series. A. C. Cope and C. M. Hofmann (*J. Amer. Chem. Soc.*, 1941, **63**, 3456—3459; cf. A., 1941, II, 161).—Heating RCHO, $CH_2Ac{\cdot}CO_2R'$, piperidine (I), AcOH, and C_6H_6 with continuous removal of H_2O gives 71—89% of *Et α-acetyl-* (II), b.p. 118—120°/18 mm. [also obtained by adding (I) in a little MeOH to $Pr^\alpha CHO$ and $CH_2Ac{\cdot}CO_2Et$ at 5—10° and then keeping at 0°], α-acetyl-δ-methyl- (III), b.p. 120—121°/15 mm., and *α-acetyl-γ-ethyl-*, b.p. 122—123°/11 mm., -Δ^α-n-*hexenoate*, *Pr$^\beta$ α-acetyl-* (IV), b.p. 125—128°/24 mm., and *α-acetyl-δ-methyl-* (V), b.p. 135—136°/24 mm.,

-Δ^{α}-n-*hexenoate*, and *Et α-acetyl-γ-ethyl-*Δ^{α}-n-*octenoate*, b.p. 138—141°/11 mm. NaOEt–EtOH at −5° converts (II) and (III) into the enolates, which with MeI at the b.p. give Et α-methyl-, b.p. 65—66°/13 mm., and *αδ-dimethyl-*Δ^{β}-n-*hexenoate*, b.p. 73—74°/15 mm., respectively. NaOPr$^{\beta}$–Pr$^{\beta}$OH and then MeI similarly convert (IV) and (V) into *Pr$^{\beta}$ α-methyl-*, b.p. 75—76°/18 mm., and *αδ-dimethyl-*Δ^{β}-n-*hexenoate*, b.p. 89—91°/25 mm., respectively. Failure of the ethylenic linking to migrate is probably due to the rapidity of the alkylation. Alkylation by BuI or PrI gives mixtures, probably because the slower reaction allows migration of the ethylenic linking and partial addition of EtOH to the resulting αβ-unsaturated ester. R. S. C.

Production of aliphatic dicarboxylic acids.—See B., 1942, II, 4.

Biological degradation of fatty acids by methyl oxidation. Preparation and metabolism of deuterodicarboxylic acids. K. Bernhard [with H. Steinhauser and E. Halpern] (*Helv. Chim. Acta*, 1941, **24**, 1412—1425).—Succinic (I), muconic, adipic (II), suberic, azelaic, and sebacic (III) acids are transformed when heated in D_2O containing NaOH into deuterodicarboxylic acids with sufficiently high D content for biological purposes. D enters the α-position in the mol. and is highest in (I), least in (III). D is firmly united and the isotopic concn. is unchanged when the neutralised acids are heated in much H_2O. Conversely Na salts of dicarboxylic acids do not acquire D appreciably in 5 at.-% D_2O. Administration of large amounts of $(\cdot CH_2 \cdot CO_2NH_4)_2$ to a dog is not followed by the appearance of the acid in the urine. After administration of deuterosuccinic acid to rats there is an appreciable accumulation of D in the body liquids, thus giving a further proof of the rapid and complete combustion of the compound. Conversion into fatty acids does not occur and the liver fatty acids of the animals contain little D. Experiments on dogs and, in one case, on rats show that the [D] of the heavy compounds is unchanged by their passage through the body. (II) is little used by rats and its decomp. in the fatty tissue does not appear to occur. Since the animals received fat and did not appreciably alter in wt. during the experiments a normal fat degradation may be assumed. The diet was also rich in carbohydrates. With help of D therefore it is conclusively shown that the difficultly combustible dicarboxylic acids with 6—10 C are not formed in appreciable amount as intermediate products of normal fat degradation. Verkade's hypothesis that all saturated fatty acids burn through dicarboxylic acids cannot be maintained. Apparently it is mainly the acids with 8—11 C which undergo partial Me oxidation to the corresponding dicarboxylic acids. As long as there is no experimental evidence to the contrary Knoop's theory of β-oxidation is the best representation of the degradation of fats *in vivo*. H. W.

***cis–trans* isomerisations. I. Mechanism of a catalysed isomerisation of maleic acid to fumaric acid. II. Mechanism of the amine-catalysed isomerisation of diethyl maleate.**—See A., 1942, I, 149.

Formation of adipic acid by oxidative degradation of the diaminocarboxylic acid derived from biotin. K. Hofmann, D. B. Melville, and V. du Vigneaud (*J. Amer. Chem. Soc.*, 1941, **63**, 3237—3238).—The diamino-acid obtained by degradation of biotin is oxidised by HNO_3 or $KMnO_4$ to adipic acid. R. S. C.

Preparation of *d*-tartaric acid.—See B., 1942, II, 4.

Mechanism of addition and condensation reactions of carbonyl compounds.—See A., 1942, I, 149.

Mechanism of the Cannizzaro reaction and some allied processes. J. Weiss (*Trans. Faraday Soc.*, 1941, **37**, 782—791).—A mechanism of the Cannizzaro reaction, based on the Haber–Willstätter theory, and supported by experimental evidence, assumes the formation of the radicals RCO and RCH·OH, and involves only electron and H atom transfers for which the energy requirements are fulfilled. The action of alkoxides on aldehydes and the benzoin synthesis are discussed from the same point of view. F. L. U.

Statistics of intramolecular aldol condensations in unsaturated ketone polymerides.—See A., 1942, I, 147.

Decomposition of ozonides with Raney nickel. N. C. Cook and F. C. Whitmore (*J. Amer. Chem. Soc.*, 1941, **63**, 3540).—The ozonides from C_9H_{18} (from CH_2Bu^{γ}·CMeEt·OH) with Raney Ni in pentane give exothermally and later at 155—120° 75% of aldehydes + ketones (MeCHO, COMe·CH_2Bu^{γ}, COEt·CH_2Bu^{γ}, and traces of CH_2O and $Bu^{\gamma}CHO$). R. S. C.

Synthesis of ketones, COR·CHR_2, from αα-disubstituted β-keto-esters. Extension of the acetoacetic ester type of ketone synthesis. B. E. Hudson, jun., and C. R. Hauser (*J. Amer. Chem. Soc.*, 1941, **63**, 3163—3164).—Condensation of CHRR′·CO_2Et with R″COCl by $NaCPh_3$ and fission of the product by H_2SO_4–AcOH–H_2O or, for more resistent esters, HI–AcOH gives 69—81% of COR″·CHRR′. *Bu$^{\beta}$ CHMeEt ketone*, b.p. 165—167°, is described. R. S. C.

Exchange reaction of diacetyl with deuterium oxide.—See A., 1942, I, 147.

Mechanism of elimination reactions. I. Decomposition of quaternary ammonium bases and xanthate esters. P. G. Stevens and J. H. Richmond (*J. Amer. Chem. Soc.*, 1941, **63**, 3132—3136).—The following results are held to confirm the view that decomp. of quaternary NH_4 compounds and xanthates normally proceeds by elimination of a proton from the β-position (or, for xanthates in which no β-H is available, by γ-elimination) (Ingold's E_2 mechanism), but that such elimination is preceded by formation of a linking between the H involved and the anion of quaternary compounds (an " intermol." linking) or the S of xanthates (an intramol. linking). The difference in behaviour between quaternary hydroxides and halides is due to the lower tendency of the halide ion than of OH′ to form H linkings. Pinacolone and HCO_2NH_4 at 125—175° give CHMeBu$^{\gamma}$·NH_2 (66%) [and 5—10% of a *sec.* amine, b.p. 86° (picrate, m.p. 180°; phenylcarbamide, m.p. 175°], converted by MeI–NaOH into dimethylpinacolylamine (I), b.p. 129—130°/759 mm. (hydriodide, m.p. 260—261°; *picrate*, m.p. 214°), which with MeI–C_6H_6 gives *trimethylpinacolylammonium iodide*, m.p. 260°. Transformation into the hydroxide and decomp. thereof at 25—30°/15—20 mm. (later 0·01—0·005 mm.) gives only CH_2:CHBu$^{\gamma}$ and NMe_3, but at 100—160° 52% of (I) + MeOH is also formed; absence of rearrangement excludes fission by way of a free radical. Formation of methylene-Δ^2-*cyclo*butene from 1 : I-dimethyl-2-methylenepyrrolidinium hydroxide (von Braun *et al.*, A., 1928, 770) by way of CH_2:C:CH·[CH]$_2$·NMe_3}OH probably proceeds by preliminary rearrangement thereof to CH_2:CH·CH:CH·CH_2·NMe_3}OH.

OH·[CHMe]$_2$·ONa (prep. from the glycol by Na in boiling PhMe) with boiling CS_2 and later MeI at room temp. gives OH·[CHMe]$_2$·O·CS_2Me, which at 200° gives *βγ-butylene thiocarbonate*, $(CHMe\cdot O)_2CS$, b.p. 87°/8 mm. [? with some thiolcarbonate, $CHMe\cdot O\diagdown$ $CHMe\cdot S\diagup$>CO], + MeOH with a little COMeEt + COS + MeSH. Contrary to Kursanov (A., 1928, 1372), $CHPh_2$·O·CS_2Me at ~330°/1 atm. gives $(CHPh_2)_2$ (30), CH_2Ph_2 (58%), CS_2, and a little MeSH and COS; in this case no β- or γ-H is available and decomp. probably proceeds by way of $CHPh_2$· and ·O·CS_2Me. R. S. C.

Micro-determination of arginine.—See A., 1942, II, 160.

Methylaspartic acids and their methylation. H. D. Dakin (*J. Biol. Chem.*, 1941, **141**, 945—950).—NHBz·$CH(CO_2Et)_2$ is converted by NaOEt and CHMeBr·CO_2Et in boiling EtOH followed by acid hydrolysis into BzOH and *β-methylaspartic* [*α-amino-β-methylsuccinic*] *acid* (I), m.p. 274—275° (decomp.), the *Cu* salt of which is freely sol. in H_2O. (I) or α-methylaspartic [α-amino-α-methylsuccinic] acid (II) is converted by Me_2SO_4 and 33% NaOH into ~70% of the theoretical amount of mesaconic acid (III) with $(NMe_4)_2SO_4$. The betaines of the two acids may be obtained on pptn. with phosphotungstic acid but on decomp. with $Ba(OH)_2$ are decomposed with formation of additional (III) (~30% of the theoretical amount) and NMe_3. Hydrolysed casein on methylation gives fumaric acid equiv. to 4·7—4·93% of aspartic acid; (III) could not be detected and it is concluded that neither (I) nor (II) is among the NH_2-acids derived from casein. H. W.

Synthesis of pantothenic acid and [its] derivatives. S. A. Harris, G. A. Boyack, and K. Folkers (*J. Amer. Chem. Soc.*, 1941, **63**, 2662—2667).—OH·CH_2·CMe_2·CH(OH)·CO_2Na (I) with Ac_2O–NaOAc gives the acid diacetate, the chloride ($SOCl_2$) of which with warm NH_2·[CH_2]$_2$·CO_2Et (II) alone gives *Et pantothenate acetate*, hygroscopic, but with (II) in warm C_5H_5N gives also some diacetate. With boiling Ac_2O, (II) gives 67% of *α-acetoxy-ββ-dimethylbutyrolactone* (III), m.p. 44—45°, $[\alpha]_D^{29}$ −13·1° in 95% EtOH, and 12% of acid diacetate; treatment of the crude product with $SOCl_2$ gives (III). *p*-NO_2·C_6H_4·CO_2·CH_2·CMe_2·CO_2H [prep. from (I) and *p*-NO_2·C_6H_4·COCl in C_5H_5N] and NH_2·[CH_2]$_2$·CO_2Na (IV) at 100° give *pantothenic acid* p-*nitrobenzoate* (V), m.p. 137—138°, $[\alpha]_D^{29}$ +4·5° in 95% EtOH. α-Hydroxy-ββ-methylbutyrolactone (VI), antipyrine (VII), and $COCl_2$ in C_6H_6 with, later, CH_2Ph·OH and additional (VII) give the *carbobenzyloxy*-derivative, m.p. 78°, $[\alpha]_D^{29}$ +12·3° in 95% EtOH, of the lactone, which with (IV) gives CH_2Ph·O·CO·NH·[CH_2]$_2$·CO_2H, m.p. 103°, and with (II) at 100° gives the *carbobenzyloxy*-ester, b.p. 140—150°/4 × 10^{-6} mm., of Et pantothenate. NH_3–H_2O or –EtOH converts (VI) into *NH_4 αγ-dihydroxy-ββ-dimethylbutyrate*, m.p. 135—136°, but liquid NH_3 at 25° gives the *amide*, m.p. 92—94°, $[\alpha]_D^{29}$ +30·9° in H_2O [*αγ-diacetate* (VIII), $[\alpha]_D^{25}$ +6·8° in Et_2O, −0·7° in $CHCl_3$, −10·3° in H_2O, −3·2° in abs. EtOH, +5·7° in EtOAc, −5·4° in dioxan]. C_5H_{11}·O·NO in AcOH converts (VIII) into the *acid diacetate*, $[\alpha]_D^{25}$ −2·6° in MeOH, ±0° in Et_2O, which with $SOCl_2$ at 100° and then (II)–C_5H_5N gives *Et pantothenate diacetate*, $[\alpha]_D^{25}$ +24·2° in Et_2O, hydrolysed by 0·5*N*-$Ba(OH)_2$ at 25° to pantothenic acid. Et pantothenate, its acetate, and (V) are inactive in microbiological tests, but the first two are active in rats and chicks. R. S. C.

Preparation and properties of sodium *d*-pantothenate. H. C. Parke and E. J. Lawson (*J. Amer. Chem. Soc.*, 1941, **63**, 2869—2871).—*l-* and *dl-α*-Hydroxy-ββ-dimethyl-γ-butyrolactone in boiling aq. $Ba(OH)_2$ give Ba (+)-, m.p. 213—215°, $[\alpha]_D^{34}$ +7·4° in H_2O, and dl-*αγ-dihydroxy-ββ-dimethylbutyrate*, +H_2O, converted by aq. Na_2SO_4 into the (+)- (I), dimorphic, m.p. 166—171° (hygroscopic) and 99—101° (not hygroscopic), $[\alpha]_D^{29}$ +8·4° in H_2O, and dl-*Na* (II)

salts, respectively. In liquid NH_3 the lactones give dl- (**III**), m.p. 127°, and (+)-*αγ-dihydroxy-ββ-dimethylbutyramide*, m.p. 92—94° (93—94°), $[\alpha]_D^{24}$ +30·8° in H_2O, +52° in MeOH (also obtained by NH_3–MeOH at room temp.). Fusion of (**II**) with β-alanine at 175° (later 150°) (91% yield) or of (**III**) with the Na salt (**IV**) of β-alanine at 100° (70% yield) gives Na *dl*-pantothenate. Fusion of (**I**) with β-alanine at 180° (61% yield) or heating the *l*-lactone with (**IV**) in $Pr^{\beta}OH$ (91% yield) gives Na *d*-pantothenate, m.p. 122—124°, $[\alpha]_D^{25}$ +27·04° in H_2O, which is less hygroscopic than is the Ca salt and more suitable as a vitamin standard. R. S. C.

Crystalline calcium pantothenate. H. Levy, J. Weijlard, and E. T. Stiller (*J. Amer. Chem. Soc.*, 1941, **63**, 2846—2847; cf. A., 1940, II, 299).—Prep. of macro-cryst. Ca (+)- and Ca (−)-pantothenate from the micro-cryst. forms is described. W. R. A.

Colorimetric test for methionine.—See A., 1942, II, 160.

Condensation reactions. II. Alkylidene-cyanoacetic and -malonic esters. A. C. Cope, C. M. Hofmann, C. Wyckoff, and E. Hardenbergh (*J. Amer. Chem. Soc.*, 1941, **63**, 3452—3456; cf. A., 1938, II, 5).—Heating $CN{\cdot}CH_2{\cdot}CO_2Et$ (0·5), $COR{\cdot}CH_2R'$ (0·55—0·6), NH_4OAc (0·05), AcOH (0·1 mol.), and C_6H_6 with continuous removal of H_2O gives good yields of $CH_2R'{\cdot}CR{:}C(CN){\cdot}CO_2Et$. Branching decreases the yield, the reaction failing with pinacolone, camphor, and anthrone. Piperidine acetate (**I**) and AcOH also effect this condensation but more slowly. AcOH–(**I**), but not AcOH–NH_4OAc, effects condensation of aldehydes with $CH_2(CO_2Et)_2$; yields are good (88—92%) with $Pr^{\beta}CHO$ or $Bu^{\beta}CHO$, and less good with other aldehydes owing to aldol condensation, but for EtCHO or $Pr^{\alpha}CHO$ Ac_2O is the best reagent. Hydrogenation (Pd–C; also Pt, Ni, or Cu chromite) of the alkylidene-esters gives 90—97% yields. Condensation of $COMe{\cdot}CH_2Ph$ with $CN{\cdot}CH_2{\cdot}CO_2Et$ by AcOH–(**I**) gives, as by-product, a little 2-*cyano*-3-*methyl*-1-*naphthol*, m.p. 200—201°, the structure of which is proved by oxidation ($KMnO_4$) to o-$C_6H_4(CO_2H)_2$, conversion by Zn dust–$ZnCl_2$–NaCl at 300° into 3 : 1-$C_{10}H_5Me{\cdot}OH$, and by prep. in 47% yield by heating $CH_2Ph{\cdot}CMe{:}C(CN){\cdot}CO_2Et$ with NH_2Ac or (**I**) at 200—220°. $Ph{\cdot}[CH_2]_3{\cdot}CO_2Et$, $CH_2Ph{\cdot}CH{:}CH{\cdot}CO_2Et$, and o-$C_6H_4Me{\cdot}CMe{:}C(CN){\cdot}CO_2Et$ are unaffected by heating in NH_2Ac, and $Ph{\cdot}[CH_2]_3{\cdot}CO_2H$ gives the amide. The following are described. Et α-cyano-β-methyl-Δ^{α}-*n*-pentenoate, b.p. 116—118°/11 mm., -hexenoate, b.p. 138—139°/19 mm., -*heptenoate*, b.p. 149—150°/19 mm., -*octenoate*, b.p. 143—145°/11 mm., and -*nonenoate*, b.p. 124—125°/2 mm. Pr^{β} *α-cyano-β-methyl-*Δ^{α}*-n-hexenoate*, b.p. 143—146°/25 mm. $CEt_2{:}C(CN){\cdot}CO_2Et$, b.p. 116—118°/9 mm. *Et α-cyano-ββ-dimethyl-*, b.p. 130—133°/12 mm., -β-*n*-propyl-, b.p. 136—137°/11 mm., -*n*- and -β-iso*butyl-*, b.p. 116—118°/3 mm., -Δ^{α}-*n-hexenoate*. Et α-cyano*cyclo*hexylideneacetate, b.p. 150—151°/9 mm. *Et α-cyano-β-n-amyl-*Δ^{α}*-n-octenoate*, b.p. 138—139°/1 mm. Et α-cyano-β-phenyl-, b.p. 136—137°/2 mm., -β-*o-tolyl-*, b.p. 141—143°/3 mm., and -γ-phenyl-β-methyl-, b.p. 139—140°/1 mm., -Δ^{α}-*n*-butenoate. Et α-cyano-β-phenyl-Δ^{α}-*n*-pentenoate, b.p. 136—138°/2 mm., -n-*hexenoate*, b.p. 135—136°/1 mm., and -n-*octenoate*, b.p. 146—148°/1 mm. *Et α-cyano-δ-phenyl-β-methyl-*n-*pentenoate*, b.p. 167—168°/3 mm. *Et α-cyano-βγ-diphenylacrylate*, m.p. 95—96°, b.p. 195—200°/3 mm. $CHR{:}C(CO_2Et)_2$, in which R = Et, b.p. 119—120°/15 mm., Pr^{α}, b.p. 122—124°/10 mm., Pr^{β}, b.p. 135—137°/27 mm., Bu^{α}, b.p. 146—147°/23 mm., and Bu^{β}, b.p. 149—150°/26 mm. *Et*$_2$ n-*hexylidenemalonate*, b.p. 162—164°/27 mm. *Et α-carbethoxy-γ-ethyl-*Δ^{α}*-n-hexenoate*, b.p. 146—148°/21 mm. *Et α-cyano-γ-phenyl*iso*valerate*, b.p. 140—142°/2 mm. R. S. C.

II.—SUGARS AND GLUCOSIDES.

Preparation of maltose monohydrate by deacetylation of maltose octa-acetate with barium methoxide. W. A. Mitchell (*J. Amer. Chem. Soc.*, 1941, **63**, 3534).—Maltose hydrate is best obtained from the octa-acetate by $Ba(OMe)_2$ (prep. described). Its reducing power $[K_3Fe(CN)_6]$ is recorded. R. S. C.

Formation of "*iso*maltose" from glucose by reversion. K. Myrbäck (*Svensk Kem. Tidskr.*, 1941, **53**, 67—77).—Treatment of glucose with cold conc. HCl gives a mixture of "*iso*maltose," (**I**), $[\alpha]_{Hg}$ +110°, and a trisaccharide (**II**), separable by fractional pptn. with EtOH. Reversion to give up to 65% of (**II**) occurs if reaction is prolonged, but the amount of (**I**) present rapidly reaches ~15% and remains const. (**I**), but not (**II**), is slowly fermentcd by yeast. The *iso*maltose produced by acid hydrolysis of starch is not formed by reversion, but its identity with (**I**) cannot be established, as the osazones of both are difficult to purify. M. H. M. A.

Emulsin. XLV. Glucosides of hydroxy-sulphonic acids and their esters. B. Helferich and H. Schnorr (*Annalen*, 1941, **547**, 201—215).—Hydrolysis of glucosides of $OH{\cdot}[CH_2]_n{\cdot}R$ by emulsin at p_H 5 is relatively little affected by increase of n from 2 to 4 if R = Cl, I, or SO_3Et, but, if R = SO_3H, there is a great increase in the rate of hydrolysis. Further, for R = SO_3H, the glucoside is readily hydrolysed by cold alkali if n = 2 but not if n = 3 or 4. γ-Chloro-*n*-propyl-β-*d*-glucoside tetra-acetate (prep. from $OH{\cdot}[CH_2]_3{\cdot}Cl$, acetobromoglucose, Ag_2O, and $CaSO_4$ in $CHCl_3$ at room temp.), m.p. 74—75°, $[\alpha]_D^{19}$ −2·50° in $CHCl_3$, with NaOMe–MeOH–$CHCl_3$ at −15° gives the free *glucoside*, m.p. 42° after sintering, $[\alpha]_D^{16}$ −29·5° in H_2O, and with NaI in dry $COMe_2$ at 85° gives *γ-iodo*-n-*propyl-*β-d-*glucoside tetra-acetate*, m.p. 61°, $[\alpha]_D^{17}$ +3·47° in $CHCl_3$, and thence (NaOMe–MeOH–$CHCl_3$ at ~−10°) the free *glucoside*, m.p. 89°, $[\alpha]_D^{16}$ −20·0° in H_2O. With aq. Na_2SO_3 at 100°, this gives *Na* n-*propyl-*β-d-*glucoside-γ-sulphonate*, m.p. 226° (corr.), $[\alpha]_D^{16}$ −25·8° in H_2O, which with Ac_2O–AcOH–C_5H_5N at 100° gives the *Na sulphonate tetra-acetate*, +2H_2O, m.p. 213—214° (corr.), $[\alpha]_D^{16}$ −22·9° in H_2O, converted by EtOH–$COMe_2$–H_2SO_4–$CHMeN_2$ into *Et* n-*propyl-*β-d-*glucoside-γ-sulphonate tetra-acetate*, m.p. 107—108°, $[\alpha]_D^{17}$ −13·2° in $CHCl_3$. NaOMe–MeOH–$CHCl_3$ at −12° then gives *Et* n-*propyl-*β-d-*glucoside-γ-sulphonate*, m.p. 96°, $[\alpha]_D^{17}$ −23·5° in H_2O, stable over NaOH–SiO_2 gel but gradually hydrolysed (SO_3Et gives SO_3H; glucoside linking unaffected) in H_2O. Similar reactions, starting from $OH{\cdot}[CH_2]_4{\cdot}OH$, lead to *δ-chloro-*, m.p. 55—57°, $[\alpha]_D^{22}$ −31·4° in H_2O [*tetra-acetate*, m.p. 104—105° (corr.), $[\alpha]_D^{22}$ −20·7° in $CHCl_3$], and *δ-iodo*-n-*butyl-*β-d-*glucoside*, m.p. 89—90°, $[\alpha]_D^{22}$ −24·8° in H_2O (*tetra-acetate*, m.p. 86—87°, $[\alpha]_D^{22}$ −20·2° in $CHCl_3$), *Na*, +$x$$H_2O$, m.p. (anhyd.) 111°, $[\alpha]_D^{22}$ (anhyd.) −25·8° in H_2O (amorphous tetra-acetate), and Et *n*-butyl-β-d-glucoside-δ-sulphonate, $[\alpha]_D^{19}$ −24° in H_2O (*tetra-acetate*, m.p. 83°, $[\alpha]_D^{22}$ −18·5° in $CHCl_3$). R. S. C.

Lignin and related compounds. LIV. Synthesis and properties of glucosides related to lignin. J. H. Fisher, W. L. Hawkins, and H. Hibbert (*J. Amer. Chem. Soc.*, 1941, **63**, 3031—3035; cf. A., 1942, II, 42).—The rates of acidic and alkaline hydrolysis of the β-*d*-xyloside of α-hydroxypropiovanillone, α-hydroxypropiovanillone, and acetovanillone, of acetovanillone β-*d*-glucoside and *β-cellobioside*, m.p. 239—240° (decomp.) (*hepta-acetate*, m.p. 208—209°), of guaiacyl and Ph β-*d*-xyloside, of Ph and *α-hydroxypropioveratrone* β-d-*glucoside*, m.p. indefinite (*tetra-acetate*, m.p. 133·6—133·8°), are determined. Presence of CO *p*- to the phenolic OH greatly increases the rate of hydrolysis of the glucoside by acid and the p_H of the phenol. Relative stabilities are: glucosides = cellobioside > xyloside. It is concluded that lignin may contain phenolic glucosides. R. S. C.

Genistin (an *iso*flavone glucoside) and its aglucone, genistein, from soya beans. E. D. Walter (*J. Amer. Chem. Soc.*, 1941, **63**, 3273—3276).—Physical properties, colour tests, crystallo-optical data, photomicrographs, and absorption spectra of genistin (**I**), genistein (isolated from soya beans), and the tri- and hexa-acetate of (**I**) are recorded. Presence of glucose in (**I**) is rigidly proved. Another flavone is also present in soya beans. R. S. C.

Synthesis of β-β′-chloroethyl-gentiobioside and -primoveroside acetates. L. P. Miller (*J. Amer. Chem. Soc.*, 1941, **63**, 3342—3343).—Acetobromogentiobiose, $Cl{\cdot}[CH_2]_2{\cdot}OH$, Ag_2O, I, and $CaSO_4$ in $CHCl_3$ at room temp. give *β-β′-chloroethylgentiobioside hepta-acetate* (**I**), partial melting at 128—129°, complete at 167—168°, $[\alpha]_D^{25}$ −20·2° in $CHCl_3$. β-β′-Chloroethyl-*D*-glucoside with CPh_3Cl in C_5H_5N at room temp. and then Ac_2O at 0° gives *β-β′-chloroethyl-*D-*glucoside* 6-*CPh*$_3$ *ether* 2 : 3 : 4-*triacetate* (47%), m.p. 158—159°, $[\alpha]_D^{25}$ +30·2° in $CHCl_3$, and thence (HBr–AcOH at 0°) *β-β′-chloroethyl-*D-*glucoside* 2 : 3 : 4-*triacetate* (55%), m.p. 120—121°, $[\alpha]_D^{28}$ −17·6° in $CHCl_3$ (derived tetra-acetate, m.p. 118—119°), which with acetobromo-glucose or -*D*-xylose, Ag_2O, I, and $CaSO_4$ in $CHCl_3$ gives (**I**) or *β-β′-chloroethylprimoveroside hexa-acetate*, m.p. 176·5—177·5°, $[\alpha]_D^{27}$ −39·9° in $CHCl_3$, respectively. M.p. are corr. R. S. C.

Deoxycorticosterone β-glucoside tetra-acetate. W. S. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 3238—3239).—Small-scale prep. of cholestanol α- and β-glucoside in 35—40 and 52—54% yield, respectively, is announced. *Deoxycorticosterone β-glucoside tetra-acetate*, m.p. 176—176·5° (corr.), $[\alpha]_D^{23\cdot6}$ +80° in $CHCl_3$, is obtained by the Helferich method. R. S. C.

Constitution of arabogalactan. I. Components and position of linkage. E. V. White (*J. Amer. Chem. Soc.*, 1941, **63**, 2871—2875).—Extraction of larch sawdust with H_2O at room temp. and pptn. by 95% EtOH gives similar fractions of arabogalactan (**I**), which is regenerated unchanged (gives furfuraldehydc equiv. to 14% of arabinose; very slightly reduces Fehling's solution) by hydrolysis of the *acetate* (20 Ac per 6 galactose + 2 arabinose units). With Me_2SO_4–aq. NaOH–N_2 at 25°, (**I**) gives a *Me*$_{20}$ derivative and thence by HCl–MeOH the *Me*$_{20}$ *ether Me*$_7$ *glucoside* and finally Me α- + β-2 : 4-dimethyl-*d*-galactoside (3 mols.; separated by insolubility in light petroleum) and a petroleum-sol. syrup (*A*) containing Me 2 : 3 : 4-tri- (1 mol.) and 2 : 3 : 4 : 6-tetra-methyl-*d*-galactoside (2 mols.) and Me 2 : 3 : 5-trimethyl-*l*-arabinoside (1 mol.). Identification of the components of (*A*) is detailed. (**I**) contains 1 : 3 and 1 : 6 O-linkings and a substantial part of the galactose is engaged at $C_{(3)}$ and $C_{(6)}$. (**I**) has a branched-chain structure, terminated by galactopyranose and arabofuranose units. R. S. C.

Fractionation of waxy and ordinary maize starch. C. G. Caldwell and R. M. Hixon (*J. Amer. Chem. Soc.*, 1941, **63**, 2876—2880).—Fractionation of maize starch by electrodialysis and freezing is described. The relative amounts of sol. and insol. products depend entirely on the extent of peptisation. The rate of crystallisation

during ageing is followed by a modification of the Sallinger process. The limit dextrins (prep. by β-amylase described) from the waxy and ordinary starch are very similar. 0·93 and 0·67% of dimethylglucose is obtained by hydrolysis of the methylated starch and limit dextrins, respectively. R. S. C.

Seed mucilages. II. Seed mucilage of *Plantago arenaria*. W. A. G. Nelson and E. G. V. Percival (*J.C.S.*, 1942, 58—61).—The seed mucilage (I) of *P. arenaria* contains ash, 5·4% (as sulphate) (3·3% after prolonged dialysis), pentosan, 90%, and uronic anhydride, 7·5%. Hydrolysis ($H_2C_2O_4$) yields *l*-arabinose 9·5%, *d*-galactose 3%, *d*-xylose 62·5%, and an aldobionic acid (12%) composed of *d*-xylose and *d*-galacturonic acid. The *Ac* derivative of (I) contains a sol. fraction, $[\alpha]_D^{17}$ −61° in $CHCl_3$. Hydrolysis (MeOH–HCl) of *methylated* (I), $[\alpha]_D^{17}$ −104° in $CHCl_3$, yields trimethylxylopyranose ~30, 2-methylxylose (*anilide*, m.p. 140°, $[\alpha]_D^{18}$ +240° in EtOAc) ~23, tetramethylgalactopyranose ~4, and a mixture, ~40%, of dimethylxylose with (?) methylated arabinoses. It is suggested that (I) has a basic mol. unit with 9 xylo- and 1 galacto-pyranose end-groups, 10 xylopyranose linking units joined by 1 : 2-β-linkings, 3 arabinose linking units, 8 xylose residues at branching points with free OH groups at $C_{(2)}$, and 2 galacturonic acid residues. A. Li.

Constitution of starch synthesised *in vitro* by potato phosphorylase. W. N. Haworth, R. L. Heath, and S. Peat (*J.C.S.*, 1942, 55—58).—The granular starch prepared from glucose 1-phosphate and potato phosphorylase (Hanes, A., 1940, III, 826) with Me_2SO_4 yields a *methylated starch*, $[\alpha]_D^{20}$ +203° in $CHCl_3$, hydrolysed (MeOH–HCl) to 2 : 3 : 6-trimethyl- with >1·5% of tetramethyl-glucose. From these results and measurements of η, a laminated structure is suggested, each unit having 80—90 glucose residues, joined by 1 : 4-α-linkings. A. Li.

Fermentability of corn-starch products : relation to starch structure. R. W. Kerr and N. F. Schink (*Ind. Eng. Chem.*, 1941, **33**, 1418—1421).—Contrary to the usually accepted ideas, starches are heterogeneous and are not composed of a single type of common mol. At least two fundamentally different chemical configurations must exist in maize starch, and although both are built up from α-glucoside linkings, probably only one is composed of 1 : 4-glucoside or maltose-type linkings. Attention is drawn to certain facts that support these principles. The total reducing sugar and fermentability of syrups made by the diastatic conversion of maize starch are not increased by acid pretreatment of the starch or by subsequent acid hydrolysis of the syrup. R. G. W.

Electrodialysis and electrophoresis in starch research. M. Samec [with C. Nučič and V. Pirkmaier] (*Kolloid-Z.*, 1941, **94**, 350—358).—Summary and bibliography. F. L. U.

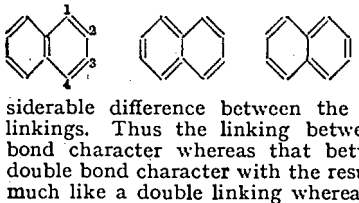
Hydrocolloidal cellulose and cellulose hydrosols.—See A., 1942, I, 143.

III.—HOMOCYCLIC.

Di*cyclo*hexylidene-2 : 2′-sulphone. O. Grummitt and C. Helber (*J. Amer. Chem. Soc.*, 1941, **63**, 3236).—Di-Δ¹-*cyclo*hexenyl (I) and a little quinol in liquid SO_2 at 100° give 50% of *di*cyclo*hexylidene*-2 : 2′-*sulphone* (II), m.p. 76—77°, which at 110—120° regenerates (I) and SO_2. R. S. C.

Production of aromatic hydrocarbons from mixtures of paraffins and *cyclo*paraffins.—See B., 1942, II, 5.

Fixation of aromatic double bonds. S. Rangaswami and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, **14**, **A**, 547—571).—Review of the literature leads to the conclusion that there is sufficient justification for concluding in favour of fixation of the double linkings in C_6H_6, $C_{10}H_8$, anthracene (I), phenanthrene (II), hydrindene, tetrahydronaphthalene, fluorene, dibenzfuran, xanthone, and xanthene, and quinoline and *iso*quinoline. This fixation seems to be of varying degrees, being very weak when chelate rings are the cause of fixation, more prominent when heterocyclic rings are involved, and more or less rigid in polynuclear aromatic structures such as $C_{10}H_8$, (I), etc. The objection that C_6H_6 and $C_{10}H_8$ have absolutely plane, symmetrical structures appears to be overcome by an application of the theory of resonance. For $C_{10}H_8$ three stable valency bond structures can be formulated, as a consequence of which there is considerable difference between the characteristics of the different linkings. Thus the linking between $C_{(1)}$ and $C_{(2)}$ has ⅔ double bond character whereas that between $C_{(2)}$ and $C_{(3)}$ has only ⅓ double bond character with the result that the former behaves very much like a double linking whereas the latter has very little such characteristics. The result is a great difference in reactivity giving rise to "fixation." In the cases of (I) and (II) the differences between the linkings are even greater owing to the existence of larger nos. of valency bond structures and it may be expected that the differences between the linkings will be further accentuated by the presence of substituents which can produce powerful electrometric effects (OH, NH_2, Br, NO_2). Similar explanations can be given of the effect of heterocyclic and chelate rings. This fixation can never be absolutely rigid since the other linkings also have very small but nevertheless appreciable double bond characteristics. When the more reactive positions are protected, the feebler reactivity of the others is exhibited particularly with powerful reagents and under favourable conditions. H. W.



So-called Dewar formula for benzene. T. S. Patterson (*Chem. and Ind.*, 1942, 54).—Seven formulæ for C_6H_6 were suggested by Dewar (*Proc. Roy. Soc. Edin.*, 1866—1869, **6**, 82), and the adoption of one particular formula as the "Dewar formula" is questioned. A. T. P.

Kinetics and mechanism of electrophilic benzene substitution reactions.—See A., 1942, I, 148.

Mechanism of the Friedel–Crafts reaction. F. Fairbrother (*Trans. Faraday Soc.*, 1941, **37**, 763—769).—When *cyclo*hexane solutions of $AlBr_3$ and EtBr are mixed there is a large increase in the dielectric polarisability, which is not shown if PhBr is used in place of EtBr. This probably indicates the formation of an ion-pair of high dipole moment. This evidence reinforces that afforded by the radio-isotopic exchange of halogen atoms between org. and inorg. halogenides (cf. A., 1937, I, 320; 1941, I, 336) in favour of the conversion of the covalent C–halogen bond into an ionic bond, through complex formation with the catalyst. F. L. U.

Use of amalgamated aluminium as catalyst in the Friedel–Crafts reaction. L. I. Diuguid (*J. Amer Chem. Soc.*, 1941, **63**, 3527—3529).—C_6H_6, RCl, and Al–Hg (activated by a little RCl) at room temp. give the following yields of PhR : PhEt 76; PhPr$^\alpha$ 15·2 + PhBr$^\beta$ 52·2 (from Pr$^\alpha$Cl); PhPr$^\beta$ 83·3 (from Pr$^\beta$Cl); CPhMeEt 36·6 + PhBu$^\alpha$ (from Bu$^\alpha$Cl); CPhMe$_3$ 59·9 (from CHMeEtCl) or 74·5% (from Bu$^\gamma$Cl). α-$C_{10}H_7$·CHMeEt (48%) is similarly obtained from CHMeEtCl. R. S. C.

Vapour-phase nitration of toluene. J. L. Bullock and E. T. Mitchell (*J. Amer. Chem. Soc.*, 1941, **63**, 3230—3231).—PhMe–HNO_3–H_2O (1 : 0·7 : 1) at 150° gives *o*- 55·7—55·9, *m*- 5·0, and *p*-$C_6H_4Me{\cdot}NO_2$ 39·1—39·3%. More HNO_3 (1 : 1·2 : 1) or interaction at 250° gives very similar proportions. R. S. C.

Mechanism and kinetics of aromatic side-chain substitution.—See A., 1942, I, 148.

Identification of organic compounds. IV. Chlorosulphonic acid as reagent for identification of alkylbenzenes. E. H. Huntress and J. S. Autenrieth (*J. Amer. Chem. Soc.*, 1941, **63**, 3446—3448; cf. A., 1940, II, 242).—Alkylbenzenes are converted by $ClSO_3H$ into sulphonyl chlorides, which with $(NH_4)_2CO_3$ give the sulphonamides. Structures of the monoalkyl-amides are proved by oxidation ($KMnO_4$) to *p*-$CO_2H{\cdot}C_6H_4{\cdot}SO_3H$. Sulphones are formed as by-products as follows : Ph_2SO_2 27, (*p*-$C_6H_4Me)_2SO_2$ 1—10, (*p*-$C_6H_4Et)_2SO_2$ 1—6, (*p*-$C_6H_4Pr^\beta)_2SO_2$ 2—3, others 0%. The following are described : $PhSO_2{\cdot}NH_2$, m.p. 150—150·5°; *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$, m.p. 135·5—136°; p-*ethyl*-, m.p. 109—110°, p-n-, m.p. 107—108°, and p-iso-*propyl*-, m.p. 104·5—105·5°, p-n-, m.p. 94·5—95°, p-sec.-, m.p. 81—82·5°, p-tert.-, m.p. 136—137°, and p-iso-*butyl*-, m.p. 84—85°, p-n-, m.p. 85·5—86·5°, and p-tert.-*amyl*-, m.p. 83—84°, p-n-*hexyl*-, m.p. 85—85·5°, p-n-*nonyl*-, m.p. 94·5—95°, p-n-*undecyl*-, m.p. 95·7—96·2°, p-cyclo*hexyl*-, m.p. 160—160·5°, 3 : 4-, m.p. 143—144°, 2 : 4-, m.p. 136·5—137°, and 2 : 5-*dimethyl*-, m.p. 145·5—146·5°, 2 : 4 : 5-, m.p. 175—176°, and 2 : 4 : 6-*trimethyl*-, m.p. 141·5—142·5°, 2-*methyl*-5-iso*propyl*-, m.p. 114·5—115·5°, ? 2 : 4-*diethyl*-, m.p. 98—99°, ? 2 : 4-*dimethyl*-5-*ethyl*-, m.p. 147—148°, 2 : 3 : 4 : 5-, m.p. 183·5—184°, 2 : 3 : 4 : 6-, m.p. 141·5—142°, and 2 : 3 : 5 : 6-*tetramethyl*-, m.p. 153—154°, ? 2 : 4-*dimethyl*-5-n-*propyl*-, m.p. 90—93°, ? 2 : 4-*dimethyl*-5-iso*propyl*-, m.p. 155·5—156°, 2 : 4 : 6-*trimethyl*-3-*ethyl*-, m.p. 131—132°, *pentamethyl*-, m.p. 182—183°, ? 2 : 4-*dimethyl*-6-tert.-*butyl*-, m.p. 132—133°, 2 : 4 : 6-*triethyl*-, m.p. 118—118·5°, 2 : 5-*di*-tert.-*butyl*-, m.p. 135·5—136·5°, and 2 : 3 : 5 : 6-*tetra*iso*propyl*- [prep. from the chloride by NH_3 in light petroleum, not by $(NH_4)_2CO_3$], m.p. 154·5—155°, -*benzenesulphonamide*; 2 : 3 : 5 : 6 : 1-$C_6HPr^\beta_4{\cdot}CO_2R$, in which R = Me, m.p. 126—126·5°, and Et, m.p. 99—99·5°; *p*-$C_6H_4Me{\cdot}SO_2Cl$, m.p. 64—66°; 3 : 4-*dimethyl*-, m.p. 52°, 2 : 4 : 6-*trimethyl*-, m.p. 50—53°, p-tert.-*butyl*-, m.p. 80—82°, 2 : 3 : 4 : 5-, m.p. 72—73°, and 2 : 3 : 5 : 6-*tetramethyl*-, m.p. 98—99°, *pentamethyl*-, m.p. 77—78·5°, ? 2 : 4-*dimethyl*-6-tert.-*butyl*-, m.p. 65—67°, p-cyclo*hexyl*-, m.p. 51—52·5°, and 2 : 3 : 5 : 6-*tetra*iso*propyl*-, m.p. 141·5—142°, -*benzenesulphonyl chloride*. R. S. C.

Action of aluminium chloride on aromatic hydrocarbons. III. Polyethyl- and tetramethyl-benzenes. (Miss) D. Nightingale and F. Wadsworth (*J. Amer. Chem. Soc.*, 1941, **63**, 3514—3517; cf. A., 1940, II, 160).—*as*- and *s*-$C_6H_3Et_3$ are partly converted into one another by $AlCl_3$ at 70—75°. 1 : 2 : 3 : 4-$C_6H_2Et_4$ gives a 1 : 1 mixture of 1 : 2 : 3 : 5- (I) and 1 : 2 : 4 : 5-isomeride. Prehnitene gives 83% of *iso*durene and 17% of durene. In all cases some higher and lower alkylbenzenes are also formed. C_6HEt_5 and, very readily, C_6Et_6 are dealkylated by $AlCl_3$. *s*- or *as*-$C_6H_3Et_3$ with EtCl–$AlCl_3$ at 20—21° gives $C_6H_2Et_4$ containing mainly (I). R. S. C.

Preparation of the chlorodinitrobenzenes from the corresponding dinitroanilines. L. H. Welsh (*J. Amer. Chem. Soc.*, 1941, **63**, 3276—3278).—Prep. of 2 : 3 : 1- (**I**) (30%), 2 : 5 : 1- (**II**) (12%), and 3 : 4 : 1-$(NO_2)_2C_6H_3$·NHAc (8·8%) and a dark solid from *m*-NO_2·C_6H_4·NHAc by HNO_3 (*d* 1·5) in H_2SO_4 at −5° to 0°, rising to 45°, and hydrolysis of (**I**) and (**II**) by conc. H_2SO_4 at 115° are described. The 6 dinitroanilines are converted into $C_6H_3Cl(NO_2)_2$ in 63—77% yield by NO·SO_3H–H_2SO_4–H_3PO_4 at −2° to 2° and then CuCl–HCl at 10° (later 80°); purification is effected by washing with conc. H_2SO_4 and chromatography (Al_2O_3). R. S. C.

Mechanism and kinetics of reactions involving free radicals.—See A., 1942, I, 147.

Manufacture of styrene derivatives.—See B., 1942, II, 5.

Syntheses in the carotenoid series. I. New preparation of hexatrienes. J. Schmitt (*Annalen*, 1941, **547**, 103—115).—In connexion with the possibility of synthesising β-dihydrocarotene and thence β-carotene, the interaction of the Mg derivative (**I**) of Br·$[CH_2]_4$·Br with ketones and aldehydes has been investigated. This leads to αζ-diols, readily dehydrated to hexadienes which are easily transformed into hexatrienes. Gradual addition of $COPh_2$ to a filtered solution of (**I**) in Et_2O gives αaζζ-tetraphenylhexane-αζ-diol, m.p. 211°, converted by hot glacial AcOH into αaζζ-tetraphenyl-$\Delta^{a\varepsilon}$-hexadiene, m.p 105°, dehydrogenated by SeO_2 in gently boiling AcOH, by *p*-O:C_6H_4:O at 180°, or by Se at 300° to αaζζ-tetraphenyl-$\Delta^{a\gamma\varepsilon}$-hexatriene, m.p. 205°. Similarly (**I**) and fluorenone afford the very sparingly sol. *αζ-difluorenylhexane-αζ-diol*, m.p. 260° (decomp.), converted by $PhSO_3H$ in boiling Ac_2O into *αζ-didiphenylene-*$\Delta^{a\varepsilon}$*-hexadiene*, m.p. 211°, which with SeO_2 in boiling PhOMe–AcOH–H_2O yields αζ-didiphenylene-$\Delta^{a\gamma\varepsilon}$-hexatriene, m.p. 336°. COPhMe and (**I**) afford *βη-diphenyl*-n-*octane-βη-diol*, m.p. 160°, transformed by boiling HCO_2H into *βη-diphenyl-*$\Delta^{\beta\zeta}$*-octadiene*, b.p. 158—159°/1·5 mm., and thence by *p*-O·C_6H_4:O at 170—180° into an isomeric *-octadiene*, m.p. 64°. (**I**) and PhCHO give αζ-diphenylhexane-αζ-diol, m.p. 132°. H. W.

Preparation of Δ^8-, $\Delta^{8(14)}$-, and Δ^{14}-cholestenes. J. C. Eck and E. W. Hollingsworth (*J. Amer. Chem. Soc.*, 1941, **63**, 2986—2990).—Dehydration of cholestan-7-ol (best prepared from the ketone by Na–C_5H_{11}·OH) by $CuSO_4$ in boiling xylene containing a little $EtCO_2H$ gives Δ^8-*cholestene* (**I**), m.p. 85—86°, $[\alpha]_D^{18}$ +11·2° in CCl_4; in absence of $EtCO_2H$ some $\Delta^{8(14)}$-*cholestene* (**II**), m.p. 53—54°, $[\alpha]_D^{25}$ +21·2° in CCl_4, is also formed. (**II**) is best obtained by shaking (**I**) with Pd–H_2 in EtOAc. HCl–$CHCl_3$ at 0° converts (**I**) or (**II**) into Δ^{14}-*cholestene* (**III**), m.p. 73—74°, $[\alpha]_D^{21}$ +26·6° in CCl_4, and a small amount of a *cholestanol*, m.p. 119—120°, $[\alpha]_D^{22}$ +37·1° in CCl_4. The structure of (**I**) is deduced from oxidation by CrO_3–aq. H_2SO_4–AcOH–C_6H_6 to Δ^8-*cholesten-7-one*, m.p. 86·5—87·5°, $[\alpha]_D^{21}$ +3·8° in CCl_4 (absorption max. at 251 mμ.) (and a *diketone*, $C_{27}H_{44}O_2$, m.p. 74—75°, $[\alpha]_D^{24}$ −53·8° in CCl_4), reduced by Na–C_5H_{11}·OH to cholestan-7-one. Structures of (**II**) and (**III**) follow by analogy with other series and are confirmed by relationships of [α]. Hydrogenation of (**III**) gives cholestane [for (**I**) and (**II**) cf. above]. >1 mol. of Br is consumed by (**I**), (**II**), or (**III**) owing to liberation of HBr, but the exact amount depends on the solvent. ~2 mols. of BzO_2H are consumed by (**I**), (**II**), or (**III**). R. S. C.

Formation of an azulene on zinc dust distillation of pyrethrosin. M. S. Schechter and H. L. Haller (*J. Amer. Chem. Soc.*, 1941, **63**, 3507—3510).—Pyrethrosin (**I**) and Zn dust at ~300—550° give 1·5% of *pyrethrazulene*, a blue oil, possibly CMe<CH:C·CMe:CH>CH, CH:C·CMe:CH

since its absorption spectrum very closely resembles that of vetivazulene and its *s*-$C_6H_3(NO_2)_3$ *compound*, sinters at 165—166°, m.p. 167—168°, with $KMnO_4$ yields AcOH as sole acidic product. With PtO_2–H_2 in AcOH, (**I**) yields *tetrahydropyrethrosin*, m.p. 231—232°. R. S. C.

Purification of anthracene. O. C. Dermer and J. King (*J. Amer. Chem. Soc.*, 1941, **63**, 3232).—Anthracene is purified by conversion into the (:CH·CO)$_2$O adduct and regenerated therefrom by sublimation from soda-lime. R. S. C.

Invert soaps of naphthalene. J. B. Niederl and H. Weingarten (*J. Amer. Chem. Soc.*, 1941, **63**, 3534—3535).—β-$C_{10}H_7$·NH_2 (**I**) and *n*-$C_{16}H_{33}Br$ in hot EtOH give N-*cetyl-β-naphthylamine*, m.p. 64° (*hydrobromide*, m.p. 161°), converted by hot MeI–K_2CO_3–EtOH into *β-naphthyldimethylcetylammonium iodide*, m.p. 106°. Bu^aBr and (**I**) in boiling BuOH give oily β-$C_{10}H_7$·$NHBu^a$, converted by boiling Bu^aBr into oily β-$C_{10}H_7$·NBu^a_2, which with MeI at room temp. gives *β-naphthylmethyldi-*n*-butylammonium iodide*, m.p. 157°. With an excess of Me_2SO_4 at 120°, (**I**) gives *β-naphthyltrimethylammonium methosulphate*, m.p. 288°. The PhOH coeff. of the quaternary salts is >0·2. R. S. C.

Interaction of betaine with primary aromatic amines, organic disulphides, and sodium sulphite. F. Challenger, P. Taylor, and (in part) B. Taylor (*J.C.S.*, 1942, 48—55).—Betaine (**I**) (free from hydrochloride) and NH_2Ph (reflux) give NHPh·CO·CH_2·NHPh, new m.p. 111—112° [*N*-NO-derivative, new m.p. 142—143° (decomp.)], NHPhMe, and NMe_3, but no NH_3, $NHMe_2$, or NH_2Me. (**I**) and *p*-C_6H_4Me·NH_2 similarly yield *p*-toluidinoacet-*p*-toluidide, new m.p. 133—134° [*NO*-derivative, m.p. 156—159° (decomp.)], and *p*-C_6H_4Me·NHMe; in some experiments a *base*, (?) (*p*-C_6H_4Me·NH·CO·CH_2)$_2$NMe, m.p. 143—144°, was also obtained. *p*-NH_2·C_6H_4·OR (R = Me, Et) affords *p*-anisidinoaceto-*p*-anisidide, m.p. 131—132° [N-*NO*-compound, m.p. 155—159° (decomp.) (rapid heating)], or *p*-phenetidinoaceto-*p*-phenetidide, m.p. 137—138°, and *p*-NHMe·C_6H_4·OR. β-$C_{10}H_7$·NH_2 and (**I**) at 200—220° yield β-$C_{10}H_7$·NHMe. (**I**) and Ph_2S_2 (reflux) afford an oil (contains PhSMe), converted by 3% aq. $KMnO_4$ at 100° into $PhSO_2Me$. $(Bu^aS)_2$ yields $MeSBu^a$, and (*n*-C_5H_{11}·S)$_2$ affords similarly MeS·C_5H_{11}-*n*. Oxidation (H_2O_2–AcOH at 100°) of the corresponding pure sulphide gives *methyl*-n-*butyl-*, m.p. 29—30°, or -n-*amylsulphone*, m.p. 35—36°, respectively. $^+NEt_3$·CH_2·CO_2^- and NH_2Ph (reflux) afford NHPhEt. No apparent reaction is observed with methionine and NH_2Ph at 190—210°. Only a little NHPhMe is isolated from NH_2Ph and paraformaldehyde (**II**) at 130—210°. (**I**) heated with Na_2SO_3 in CO_2 yields Me_2S, but no odour of Me_2Se or Me_2Te is observed when (**II**) is heated at 270° with Na_2SeO_3 or K_2TeO_3, respectively. Theoretical aspects are discussed. A. T. P.

Restricted rotation in arylamines. II. Preparation and resolution of *N*-β-carboxypropionyl-*N*-ethyl-3-bromomesidine and 4-*N*-β-carboxypropionyl-*N*-alkylamino-5-alkoxy-1 : 3-dimethylbenzenes. R. Adams and H. W. Stewart (*J. Amer. Chem. Soc.*, 1941, **63**, 2859—2864; cf. A., 1940, II, 339).—Mesidine is obtained from the NO_2-compound by Raney Ni–H_2 at 2—3 atm. Heating 1 : 3 : 5 : 4 : 2-C_6HMe_3Br·NH_2 and aq. Et_2SO_4 at ~80° (less well, 95°), conversion into the NO-derivative (*A*) by HCl–$NaNO_2$, and reduction thereof by $SnCl_2$–conc. HCl at 70—75° gives 3-*bromo*-N-*ethylmesidine* (N = 1) (**I**) (49·5%), b.p. 136—137°/4 mm.; the aq. mother-liquors from (*A*) at room temp. yield 1 : 3 : 5 : 4 : 2-C_6HMe_3Br·OH, m.p. 84—84·5° [lit. 81° (uncorr.)]. With $(CH_2$·$CO)_2O$ and a drop of H_3PO_4 in boiling C_6H_6, (**I**) gives N-β-*carboxypropionyl*-N-*ethyl*-3-*bromomesidine*, m.p. 111·5°, resolved by cinchonidine (not other bases) in EtOAc–MeOH into the d- (cinchonidine salt, m.p. 117—118°, [α] −41°) and l- (cinchonidine salt, m.p. 112·5—114·5°, [α] −66°) *-forms*, m.p. 104·5°, [α] ±25°, which in boiling Bu^aOH have a half-life ~28 hr. (cf. 9 hr. for the *N*-Me analogue, *loc. cit.*). *m*-5-Xylenol in Et_2O with aq. HNO_3 gives 36% of the 4- (**II**), m.p. 65—66°, and 25% of the 2-NO_2-compound, m.p. 108·5°. The dry Na salt of (**II**) with boiling Me_2SO_4–C_6H_6 gives 93·5% of the Me ether, m.p. 44—45°, reduced by Raney Ni–H_2 in 95% EtOH at 100°/135 atm. to 5 : 1 : 3 : 4-OMe·$C_6H_2Me_2$·NH_2 (**III**) (98·5%), m.p. 35·5—36·5°, b.p. 120—121°/10 mm. This yields as above 5-*methoxy*-N-*methyl*-m-4-*xylidine* (60·8%), b.p. 61—62°/1·5 mm., the N-β-*carboxypropionyl* derivative (**IV**), m.p. 153·5°, of which is resolved to the d- (cinchonidine salt, m.p. 133—136°, [α] −56°) and l- (amorphous cinchonidine salt, [α] −46°) *-forms*, m.p. 152—153°, [α] ±13°, half-life in boiling MeOAc 2·7 hr. Addition of (**IV**) to fuming HNO_3 at 0° gives the 2 : 6-$(NO_2)_2$-derivative (99·2%), m.p. 178—178·5°, which, as also the amides described below, could not be resolved although it had p_H 2·92 whereas the other amides have p_H 3·97—4·06 (0·1M. solutions in 70% EtOH). With EtBr–H_2O at room temp., (**III**) gives the N-*Et* derivative (56·1%), b.p. 61—62°/1·5 mm. (N-β-*carboxypropionyl* derivative, m.p. 133·5°). The Na derivative of (**II**) gives, as above, 4-*nitro*-5-*ethoxy*-m-*xylene*, m.p. 78·5°, 5-*ethoxy*-m-4-*xylidine*, b.p. 73—74°/1 mm. [*hydrochloride*, sublimes at 190° (decomp.)], 5-*ethoxy*-N-*methyl*-, b.p. 65—66°/1 mm. (N-β-*carboxypropionyl* derivative, m.p. 114·5°), and -N-*ethyl*-m-4-*xylidine*, b.p. 69—70°/1 mm. (N-β-*carboxypropionyl* derivative, m.p. 91·5°). M.p. are corr. [α] are $[\alpha]_D^{30}$ in abs. EtOH. R. S. C.

***N*^{1}-Silver derivatives of sulphanilamide and related compounds.** C. E. Braun and J. T. Towle (*J. Amer. Chem. Soc.*, 1941, **63**, 3523).—Addition of aq. $AgNO_3$ (1 mol.) to the Na derivatives of p-NH_2·C_6H_4·SO_2·NH_2, its N^1-Ac derivative (prep. of the Na salt by conc. aq. NaOH described), or sulphapyridine give the N^1-*Ag* salts. R. S. C.

Derivatives of sulphanilamide and cholic acid.—See A., 1942, II, 146.

Chemotherapeutic studies; preparation of substituted sulphonamides. C. Marchant, C. C. Lucas, and L. McClelland (*Canad. J. Res.*, 1942, **20**, **B**, 5—16).—*p*-Acetamidobenzenesulphonamides, *p*-NHAc·C_6H_4·SO_2·NHR, are obtained by warming equimol. quantities of the reactants with $COMe_2$ containing C_5H_5N or by melting an intimate mixture of the acid chloride (1 mol.) and amine (2 mols.). NH_2-compounds are obtained by catalytic reduction of NO_2-compounds and CO_2Et-compounds by esterifying (HCl + EtOH) the requisite acids. Ac is removed by hydrolysis with boiling acid or alkali. *Sulphanilamides*, *p*-NH_2·C_6H_4·SO_2·NHR, are thus obtained (the m.p. of the N^4-*Ac* derivatives are recorded in parentheses) in which R = *p*-, m.p. 165° (258°), *m*-, m.p. 169° (244°), and *o*-, m.p. 179° (200°) -NO_2·C_6H_4·; 3 : 6-, m.p. 199° (266·5°), and 3 : 4-, m.p. 189° (239°), -NO_2·C_6H_3Me·; 6 : 3-, m.p. 188° [261·5° (decomp.)], and 4 : 2-, m.p. 117° (175°), -OMe·$C_6H_3(NO_2)$·; *p*-, m.p. 138° (235°), *m*-, m.p. 177°, and *o*-, m.p. 208°, -NH_2·C_6H_4·; 3 : 6-, m.p. 208·5°, and 3 : 4-, m.p. 185°, -NH_2·C_6H_3Me·; 6 : 3-, m.p. 232°, and 4 : 2-, m.p. 195°, -OMe·$C_6H_3(NH_2)$·; *p*-, m.p. 190° (208°), *m*-, m.p. 133·5° (205°),

and *o*-, m.p. 155·5° (244·5°), -C_6H_4Me; *p*-, m.p. 194° (200°), *m*-, m.p. 163·5° (193°), and *o*-, m.p. 199° (212°), -$OMe{\cdot}C_6H_4{\cdot}$; *p*-, m.p. 197°, *m*-, m.p. 196° (274°), and *o*-, m.p. 226° (233°), -$CO_2H{\cdot}C_6H_4{\cdot}$; *p*-, m.p. 230°, *m*-, m.p. 105°, and *o*-, m.p. 165·5°, -$CO_2Et{\cdot}C_6H_4{\cdot}$; 2 : 6-, m.p. 231° (236·5°), and 2 : 4-, m.p. 149° (214·5°), -$C_6H_3Me_2$; 2 : 5-$OMe{\cdot}C_6H_3Me{\cdot}$, m.p. 161° (206°); 2 : 5-$C_6H_3MePr^{\beta}$, m.p. 150·5° (160·5°); *p*-C_6H_4Ac, m.p. 211° (254·5°); *p*-C_6H_4Bz, m.p. 181·5° (218·5°); *p*-C_6H_4Br, m.p. 178° (208°); $OEt{\cdot}[CH_2]_2{\cdot}$, m.p. 100° (150°); *p*-$AsO_3H_2{\cdot}C_6H_4{\cdot}$, m.p. — [275° (decomp.)]. *Disulphanilyl-p-phenylenediamine*, m.p. 263° (decomp.) [Ac_2 derivative, m.p. 316·5° (decomp.)], -*m-toluylenediamine*, m.p. 229° (Ac_2 derivative, m.p. 278°), and -*benzidine*, m.p. 290° (Ac_2 derivative, m.p. 288°), are described. M.p. are corr. H. W.

4-Amino-4′-di-β-hydroxyethylamino-2′-methylazobenzene. G. Shulman (*J. Amer. Chem. Soc.*, 1941, **63**, 3236—3237).—Coupling of m-$C_6H_4Me{\cdot}N([CH_2]_2{\cdot}OH)_2$ [prep. from m-$C_6H_4Me{\cdot}NH_2$ by $(CH_2)_2O$ at >1 atm.) with *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ in HCl–NaOAc and reduction of the product by 10% cryst. Na_2S at 90° gives *4-amino-4′-di-β-hydroxyethylamino-2′-methylazobenzene*, orange, m.p. 149°, whence blue to black dyes are obtained by diazotisation and further coupling. R. S. C.

Decomposition of arylazo-β-naphthylamines by sodium nitrite and glacial acetic acid. H. H. Hodgson and C. K. Foster (*J.C.S.*, 1942, 30—33).—Many arylazo-β-naphthylamines are converted by $NaNO_2$–AcOH at 70°, then at room temp., into the unstable diazonium acetates, which are then decomposed to the corresponding arylazo-β-naphthyl acetates. These may be partly or wholly hydrolysed by the H_2O formed in the reaction to the naphthols as with, *e.g.*, *o*-$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2$-*β*. The following are new: m-, m.p. 85°, and p-*fluoro*-, m.p. 120°, m-*chloro*-, m.p. 160°, 2 : 5-*dichloro*-, m.p. 168°, p-*iodo*-, m.p. 170°, 4-*bromo*-3-*nitro*-, m.p. 190°, 3-*nitro*-4-*methyl*-, m.p. 199°, 4-*chloro*-2-*nitro*-, m.p. 255°, 4-*bromo*-2-*nitro*-, m.p. 259°, and 3 : 5-*dinitro*-2-*hydroxy-benzeneazo-β-naphthylamine*, m.p. 274°; 4-, m.p. 214°, and 5-*nitro*-1-*naphthaleneazo-β-naphthylamine*, m.p. 212°; *benzeneazo-β-naphthyl acetate*, m.p. 117°; p-*fluoro*-, m.p. 130°, m-, m.p. 81°, and p-*chloro*-, m.p. 134°, p-*bromo*-, m.p. 136°, m-*nitro*-, m.p. 162°, 2-*nitro*-4-, m.p. 133°, and 3-*nitro*-4-*methyl*-, m.p. 157°, 4-*chloro*-2-*nitro*-, m.p. 163—164°, 4-*bromo*-2-, m.p. 160°, and -3-*nitro*-, m.p. 167°, 3 : 5-*dinitro*-2-*hydroxy*-, m.p. 184°, and p-*carboxy-benzeneazo-β-naphthyl acetate*, m.p. 206°; 4-, m.p. 155°, and 5-*nitronaphthaleneazo-β-naphthyl acetate*, m.p. 180°. A. T. P.

Preparation of aromatic sulphuric esters. J. Feigenbaum and C. A. Neuberg (*J. Amer. Chem. Soc.*, 1941, **63**, 3529—3530).—$ArKSO_4$ is best (90%; no distillation) obtained by adding, first, $ClSO_3H$ in the cold and then 50% aq. KOH to ArOH in $NPhMe_2$. For some phenols C_5H_5N is preferable to $NPhMe_2$. R. S. C.

Preparation and properties of three isomeric *n*-hexylcresols and their chlorinated derivatives. P. P. T. Sah and H. H. Anderson (*J. Amer. Chem. Soc.*, 1941, **63**, 3164—3167).—*o*-, *m*-, and *p*-Cresol with SO_2Cl_2 at room temp. (later warm) give 5-chloro-*o*- (~84%), m.p. 48—49°, b.p. 220—225°, 6-chloro-*m*- (~84%), m.p. 66°, b.p. 234—236°, and 3-chloro-*p*-cresol (77%), b.p. 195—197°. o-, b.p. 263—264°, m-, b.p. 280—283°, and p-*tolyl*, b.p. 268—270°, 5-*chloro*-o-, b.p. 280—283°, 6-*chloro*-m-, b.p. 286—288°, and 3-*chloro*-p-*tolyl*, b.p. 283—285°, n-*hexoate* (all prepared in 75—85% yield by *n*-$C_5H_{11}{\cdot}COCl$ in boiling CCl_4) with $AlCl_3$ at 140° give 3-*n*-hexoyl-*o*- (50·5%), b.p. 131—132°/1 mm., 4-*n*-hexoyl-*m*- (85%), b.p. 135—137°/2 mm., and 3-*n*-hexoyl-*p*- (62%), b.p. 132—133°/2 mm., 5-*chloro*-3-n-*hexoyl*-o- (60%), b.p. 149—151°/1 mm., 6-chloro-4-*n*-hexoyl-*m*- (76%), m.p. 42—44°, b.p. 152—154°/1 mm., and 3-*chloro*-5-n-*hexoyl*-p- (62%), b.p. 150—152°/1 mm., -*cresol*, reduced by Zn–Hg–conc. HCl–EtOH–PhMe to 3-*n*-hexyl-*o*- (70%), b.p. 130—131°/1 mm., 4-*n*-hexyl-*m*- (90%), b.p. 132—133°/1 mm., 3-*n*-hexyl-*p*- (70%), b.p. 134—135°/1 mm., 5-*chloro*-3-n-*hexyl*-o- (90%), b.p. 140—142°/2 mm., 6-chloro-4-*n*-hexyl-*m*- (80%), m.p. 27—29°, b.p. 150—152°/1 mm., and 3-*chloro*-5-n-*hexyl*-p- (75%), b.p. 137—139°/1 mm., -*cresol*. The isomeric *n*-$C_6H_{13}{\cdot}C_6H_4{\cdot}OH$ are converted into the appropriate Cl-derivatives by SO_2Cl_2–CCl_4 in 60—65% yield. Chlorination reduces the toxicity of the *n*-hexylcresols to mice. R. S. C.

Synthesis of amyl- and hexyl-α-naphthol. Y. F. Chi and C. T. Jang (*J. Amer. Chem. Soc.*, 1941, **63**, 3155—3156).—α-$C_{10}H_7{\cdot}OH$, RCO_2H, and $ZnCl_2$ give 2-n-, m.p. 75·5—76·5°, b.p. 160—168°/5 mm. (*oxime*, m.p. 115—117°; *semicarbazone*, m.p. 163—165°), and 2-iso-*valeryl*-, m.p. 65—66·5°, b.p. 150—155°/2 mm. (*oxime*, m.p. 149—151°; *semicarbazone*, m.p. 213—215°), and 2-n-*hexoyl*-, m.p. 62—63°, b.p. 180—186°/5 mm. (*oxime*, m.p. 97—99°; *semicarbazone*, m.p. 183—184°), reduced (Clemmensen) to 2-n-, m.p. 45—46·5°, b.p. 130—135°/5 mm., and 2-iso-*amyl*-, b.p. 135—140°/3 mm., and 2-n-*hexyl*-, m.p. 42—43°, b.p. 155—165°/3 mm., -1-*naphthol*, respectively. R. S. C.

Exchange reactions of 4-nitro-1-naphthyl methyl and ethyl ether with sodium ethoxide and methoxide, respectively, and the reduction of certain 1-nitronaphthalene derivatives. H. H. Hodgson and J. Habeshaw (*J.C.S.*, 1942, 45—47).—1 : 2-, 1 : 4-, or 2 : 1-$C_{10}H_6Cl{\cdot}NO_2$ and 25% KOH–MeOH at 55° afford 2 : 1- 4 : 1- or 1 : 2-$NO_2{\cdot}C_{10}H_6{\cdot}OH$, respectively, in ~90% yield, whereas replacement of Cl in *o*- or *p*-$C_6H_4Cl{\cdot}NO_2$ requires reaction under pressure. 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}OMe$ (I) in NaOEt–EtOH at 65° yields 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}OEt$ (II), reconverted by NaOMe–MeOH at 65° into (I). The use of NaOPr in similar experiments yielded amorphous substances. The mechanism of the exchange is discussed. 4 : 1-$C_{10}H_6Cl{\cdot}NO_2$ or (I) and Zn–EtOH yield 4 : 4′-*dichloro*-, m.p. 262—263°, or 4 : 4′-*dimethoxy*-1 : 1′-*azonaphthalene*, m.p. 105—107°, respectively. Conditions are established for the reduction of (I) and (II) to the amines. A. T. P.

Carboxylic acid derivatives of 4 : 4′-diaminodiphenylsulphone. W. H. Gray and B. C. Platt (*J.C.S.*, 1942, 42—45).—4 : 4′-Diaminodiphenylsulphone (I) and $Et_2C_2O_4$ yield 4 : 4′-*biscarbethoxyformamido-diphenylsulphone*, m.p. 257°, converted by hot 2·5% aq. NaOH (6 min.) into 4-*amido*-4′-*carboxyformamido*-, froths at 195°, or by hot 0·5% KOH–EtOH (15 min.) into 4 : 4′-*biscarboxyformamido-diphenylsulphone*, froths at 188° to a solid, m.p. ~275°. (I) and $CO_2H{\cdot}CH_2{\cdot}COCl$ (modified prep.) in dioxan at 65° yield 4 : 4′-*bis-carboxyacetamidodiphenylsulphone*, $+H_2O$, froths at 183° and loses CO_2 to give the 4 : 4′-$(NHAc)_2$-compound. (I) and $(CH_2{\cdot}CO)_2O$ at 170° or 225° afford 4 : 4′-*bis-β-carboxypropionamido*-, m.p. 227° (converted into the imide), or 4 : 4′-*bis-succinimido-diphenylsulphone*, m.p. 343°, respectively. δ-Carbethoxyvaleryl or η-carbomethoxy-octoyl chloride and (I) in $COMe_2$–$CaCO_3$ (reflux) yield 4 : 4′-*bis*-δ-*carbethoxyvalerimido*-, m.p. 139°, or 4 : 4′-*bis*-η-*carbomethoxyoctamido-diphenylsulphone*, m.p. 122° (free *acid*, m.p. 134°), respectively. (I) (1 mol.) and *o*-$C_6H_4(CO)_2O$ (1 mol.) at 200°, or in C_5H_5N at 100° (bath), give 4-*amino*-4′-*phthalimidodiphenylsulphone* (II), m.p. 256—258°, also obtained from *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_2Me$ with or without $ZnCl_2$; 2 mols. of *o*-$C_6H_4(CO)_2O$ in C_5H_5N give the 4 : 4′-*bisphthal-imido*-compound (III), m.p. 310°, also obtained from Me H or Et_2 phthalate. (II)–5% aq. NaOH at 100°, or (III)–0·5% KOH–EtOH, yield 4-*amino*-4′-*o*-*carboxybenzamido*-, froths at 176° [heat → (II)], or 4 : 4′-*bis*-*o*-*carboxybenzamido-diphenylsulphone*, m.p. 182° (decomp.) [heat → (III)], respectively. Camphoric anhydride and (I)–C_5H_5N (reflux) yield the 4 : 4′-*biscamphorimido*-compound ($+0·5H_2O$), m.p. 375°; pimelic, maleic, malic, glutamic, and quinolinic acid act similarly. Toxicity and coccicidal activity of the products are given. A. T. P.

Detoxication. XI. Identification of pyrocatechol-4-sulphonamide as a metabolic product of *p*-hydroxybenzenesulphonamide in the rabbit. Synthesis of derivatives of pyrocatecholsulphonamide. R. T. Williams (*Biochem. J.*, 1941, **35**, 1169—1174; cf. A., 1942, III, 334).—1 : 2 : 4-$(OH)_2C_6H_3{\cdot}SO_2H$ [from *o*-$C_6H_4(OH)_2$ and conc. H_2SO_4 at 0°] with Ac_2O in C_5H_5N, followed by PCl_5 on the resulting C_5H_5N salt, yields 1 : 2-*diacetoxybenzene*-4-*sulphonyl chloride*, m.p. 116°, which with aq. NH_3, then dil. HCl, gives pyrocatechol-4-sulphonamide (I) (a resin), and with NH_2Ar in EtOAc yields the Ac_2 derivatives, m.p. 127—128°, 153°, and 131°, respectively, of *pyrocatechol*-4-*sulphonanilide*, m.p. 225° (decomp.), -m-*chloroanilide*, m.p. 177°, and -*β-naphthylamide*, m.p. 218° (decomp.). With Me_2SO_4, *p*-$OH{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ (II) yields *anisole*-p-*sulphondimethylamide*, m.p. 75. When the urine of rabbits fed with (II) is hydrolysed (HCl), extracted with Et_2O, the extracts acetylated, and the H_2O-sol. Ac derivatives hydrolysed and methylated (Me_2SO_4) it yields *veratrole*-4-*sulphondimethylamide*, m.p. 112°, also obtained (m.p. 113° and 115°, respectively) by methylating (I) or veratrole-4-sulphonamide. A. Li.

Reactions of hydrazoic acid. I. L. H. Briggs, G. C. de Ath, and (in part) S. R. Ellis (*J.C.S.*, 1942, 61—63).—$CHPh{:}CH{\cdot}COMe$ and N_3H–$CHCl_3$–H_2SO_4 at 0°, rising to 60°, afford $CHPh{:}CH{\cdot}CO{\cdot}NHMe$, whereas $CH_2Ph{\cdot}CH_2{\cdot}COMe$ (2 : 4-*dinitrophenylhydrazone*, m.p. 131—132°) at 0° similarly yields $CH_2Ph{\cdot}CH_2{\cdot}NHAc$. $CH_2Ph{\cdot}CHMe{\cdot}COMe$ (2 : 4-*dinitrophenylhydrazone*, m.p. 81°) gives acet-β-phenyl*iso*propylamide. $CH_2Ph{\cdot}CH(CO_2H)_2$ and N_3H–$CHCl_3$–dioxan–H_2SO_4 at 40° afford *dl*-phenylalanine in 16% yield. Podocarpic acid gives an amine, $C_{16}H_{23}ON$ [*sulphate*, m.p. 279° (decomp.)], in good yield; thus there is little steric hindrance in the Schmidt reaction. Esters also react; *e.g.*, MeOBz or EtOBz and N_3H in $CHCl_3$– or C_6H_6–H_2SO_4 give ~25% of NH_2Ph. *o*-, *m*-, or *p*-Toluic acid (at 40—45°) gives yields of 46, 70, or 24%, respectively, of the corresponding toluidines. Stearic acid (in C_6H_6 at 40°) affords *n*-$C_{17}H_{35}{\cdot}NH_2$. N_3Me decomposes similarly to N_3H, but ketones and acids are unaffected during the reaction. A. T. P.

Potassium α-naphthyl*iso*propyl. R. D. Kleene (*J. Amer. Chem. Soc.*, 1941, **63**, 3539).—α-$C_{10}H_7{\cdot}CMe_2{\cdot}OH$, $NaNH_2$, and MeI in dioxan give the *Me ether*, b.p. 100—101°/3 mm., which with Na–K in Et_2O–N_2 gives α-$C_{10}H_7{\cdot}CMe_2K$, converted by CO_2 into α-1-*naphthyl*-iso*butyric acid* (32%), m.p. 121—122°. R. S. C.

Factors which greatly increase the activity of the phenolic hydroxyl group of *l*-tyrosine. D. E. Bowman (*J. Biol. Chem.*, 1941, **141**, 877—887).—The rate at which *l*-tyrosine (I) reacts with I, $KMnO_4$, or $AgNO_3$ is usually very slow but may be greatly increased by the presence of a PO_4''' buffer, small increases in p_H greatly intensifying the reaction. In the presence of PO_4''' further marked acceleration results from a moderate increase of temp. until the reaction becomes

instantaneous. This reducing action of (I) may be attributed to the phenolic OH. It appears that the normal physiological state should provide the conditions necessary to support the increased activity of this group. This may explain why this group is capable of playing such a dominant rôle in the physiological action of various protein catalysts. H. W.

Derivatives of 1-phenylcycloalkane-1-carboxylic acids. R. D. Kleene (*J. Amer. Chem. Soc.*, 1941, **63**, 3538—3539).—1-*Phenylcyclobutane*-1-*carboxyl-amide*, m.p. 75—76°, *-anilide*, m.p. 96—96·2°, *-p-toluidide*, m.p. 129—131°, and *-o-bromoanilide*, m.p. 82—83°, 1-*phenylcyclopentane*-1-*carboxyl-anilide*, m.p. 98—99°, *-p-toluidide*, m.p. 145—146°, and *-o-bromoanilide*, m.p. 75—76°, 1-*phenylcyclohexane*-1-*carboxyl-anilide*, m.p. 85—86°, *-p-toluidide*, m.p. 165—166°, and *-o-bromoanilide*, m.p. 167—169°, are prepared from the respective acid chlorides. R. S. C.

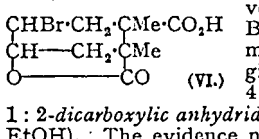
Synthesis and characterisation of *tert.*-naphthenic acids. B. Shive, W. W. Crouch, and H. L. Lochte (*J. Amer. Chem. Soc.*, 1941, **63**, 2979—2984).—*dl*-Camphor (cf. Forster, *J.C.S.*, 1896, **69**, 36, who used *l*-camphor) and Br at 100° give dl-*αα-dibromocamphor*, m.p. 54—55°, oxidised by HNO_3 (*d* 1·6) to dl-*dibromocampholide*, m.p. 138—139°, converted by Zn dust in boiling NH_3–EtOH–H_2O into dl-*bromocamphorenic acid*, m.p. 180—181°, which with Na–Hg in boiling H_2O gives dl-*camphorenic acid*, m.p. 165—166°. H_2–PtO_2 in AcOH then gives dl-*dihydrocamphorenic* [1 : 2 : 2-*trimethylcyclohexane*-1-*carboxylic*] *acid* (I), m.p. 179—180° (*amide*, m.p. 164—165°). Et 2-*iso*propyl*cyclo*hexanone-2-carboxylate and Zn–Hg–HCl give Et 1-*iso*propyl*cyclo*hexanecarboxylate (crude), b.p. 92—95°/10 mm., hydrolysed by conc. HCl at 140—150° to the *acid* (II), m.p. 104—105° (*anilide*, m.p. 101—102°). Et 2-*iso*propyl*cyclo*pentanone-2-carboxylate, b.p. 248—249°/750 mm., with boiling MgMeI–Et_2O, LiMe–Et_2O, or Mg–MeI–C_6H_6 gives a mixture, whence dehydration by boiling (1 atm.) with $KHSO_4$ gives *Et* 2-*methyl*-1-iso*propyl*-Δ^2-cyclo*pentenecarboxylate*, b.p. 221—222°/753 mm., which by hydrogenation and hydrolysis as above yields 2-*methyl*-1-iso*propyl*cyclo*pentanecarboxylic acid* (III), m.p. 52—53° (*Et* ester, b.p. 225—226°/745 mm.; *anilide*, m.p. 115—116°). Addition of 2-methyl*cyclo*pentanone and $CMe_2Br{\cdot}CO_2Et$ in Et_2O to Mg in much Et_2O gives *Et* α-*hydroxy*-α-2-*methyl*cyclo*pentyl*iso*butyrate*, b.p. 122—123°/12 mm., converted as above into *Et* α-2-*methyl*-Δ^1-cyclo*pentenyl*iso*butyrate*, b.p. 224—225°/753 mm., and α-2-*methyl*cyclo*pentyl*iso*butyric acid* (IV), b.p. 256—257°/743 mm. (*Et* ester, b.p. 225—226°/750 mm.; *anilide*, m.p. 102—103°). (I), (II), (III), and (IV) differ from an acid, $C_{10}H_{18}O_2$, obtained from Californian petroleum (Shive *et al.*), by degradation of a base therein (Roberts *et al.*), and ? from Iranian petroleum (Kennedy, B., 1940, 9). R. S. C.

Synthesis of 3 : 5-diethylbenzoic acid. H. R. Snyder, R. R. Adams, and A. V. McIntosh, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 3280—3282).—20·5% of 3 : 5 : 1-$C_6H_3Me_2{\cdot}CO_2H$ is obtained from *s*-$C_6H_3Me_3$ by HNO_3, but *s*-$C_6H_3Et_3$ gives only a little 3 : 5 : 1-$C_6H_3Et_2{\cdot}CO_2H$ (I), m.p. 130° (lit. 133°) (*Me* ester, b.p. 110—112°/3·5 mm.), with 5-*ethyl*iso*phthalic acid* (5·3%), m.p. 265—266°, and 5-*aceto*-3-*ethylbenzoic acid*, m.p. 156—157° (*Me* ester, m.p. 77—78°). PhBr, EtBr (2 mols.), and $AlCl_3$ give *p*-$C_6H_4Br_2$ and *s*-$C_6H_3Et_3$. 2 : 4 : 1-$C_6H_3Et_2{\cdot}NH_2$, b.p. 142·5°/33 mm. (prep. from 2 : 4 : 1-$C_6H_3Et_2{\cdot}NO_2$, b.p. 112—114°/3·8 mm., by Raney Ni–H_2 in EtOH at 40—60°/1000—2000 lb.; 80—90% yield), with Br–AcOH–MeOH at <15° gives 6-*bromo*-2 : 4-*diethylaniline* (55%; ~40% in large-scale runs), b.p. 100—105°/1·5 mm., the diazonium salt from which with H_3PO_2 gives 5-*bromo*-1 : 3-*diethylbenzene* (70%), b.p. 115—119°/17 mm. Prep. of (I) therefrom by Grignard reactions is unsatisfactory, but CuCN in boiling C_5H_5N (bath : 235—240°) gives 3 : 5-*diethylbenzonitrile* (67%), b.p. 147·5—149°/29 mm., whence NaOH in boiling aq. $(CH_2{\cdot}OH)_2$ gives 85% of (I). R. S. C.

Cleavage of the alkyl–oxygen bond in the hydrolysis of esters. *tert.*-Butyl 2 : 4 : 6-trimethylbenzoate. S. G. Cohen and A. Schneider (*J. Amer. Chem. Soc.*, 1941, **63**, 3382—3388).—Cleavage of the O–alkyl linking of esters occurs during methanolysis or acid hydrolysis of *tert.*-alkyl esters. $Bu^{\gamma}OBz$ in boiling MeOH (4 days) gives $MeOBu^{\gamma}$ (60·7%) and BzOH (22·6%) with MeOBz (61·9%; produced from the liberated BzOH and MeOH); the $MeOBu^{\gamma}$ is a direct product, not being formed from $Bu^{\gamma}OH$ and MeOH in presence of BzOH [or (II); cf. below]. With NaOMe (0·1 mol.) in boiling, anhyd. MeOH, $Bu^{\gamma}OBz$ gives MeOBz (71·6%) and $Bu^{\gamma}OH$ (81·7%) and no $MeOBu^{\gamma}$. *Bu*$^{\gamma}$ 2 : 4 : 6-*trimethylbenzoate* (I) (prepared in 79% yield from the acid chloride and $Bu^{\gamma}OH$ in C_5H_5N, but not from the Ag salt and $Bu^{\gamma}Cl$), b.p. 142°/13 mm., in boiling MeOH (7 days) gives $MeOBu^{\gamma}$ (12·5%) and 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CO_2H$ (II) (6·1%) with 82·5% of unchanged (I), but is unaffected by NaOMe–MeOH. Similar cleavage of the O-alkyl linking occurs with esters of primary or *sec.* alcohols and strong acids (*e.g.*, Me_2SO_4), as evidenced by alcoholysis to ROR′. Alkaline hydrolysis occurs by addition of OH^- to give an intermediate $OH{\cdot}CR(:O^-){\cdot}OR'$. Acid hydrolysis (including alcoholysis) occurs by addition of H^+ to give $HO^+{:}CR{\cdot}OR' \rightleftharpoons OH{\cdot}CR^+{:}OR'$. In (I) the C but not the O is sterically hindered; thus, (I) is almost quantitatively converted into (II) by 39·5% HCl–MeOH at 0° or boiling 18% HCl, but boiling 20% NaOH is ineffective. Related results are shown by ROAc: alkaline hydrolysis decreases as R changes from Me to Bu^{γ}, but acid hydrolysis passes through a min. and that of $Bu^{\gamma}OAc$ is ~15% faster than that of MeOAc. R. S. C.

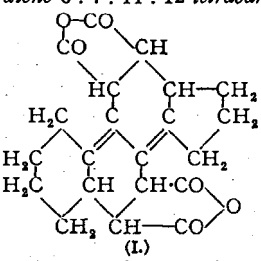
Resonance and the hindered carbonyl–Grignard reaction. I. R. T. Arnold, H. Bank, and R. W. Liggett (*J. Amer. Chem. Soc.*, 1941, **63**, 3444—3446).—Interaction of 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}COMe$ with MgRX proceeds by formation of $[C_6H_2Me_3(=CH_2{\cdot}{\cdot}{\cdot}H)=O{\cdot}{\cdot}{\cdot}MgX]^+$, and thence of $C_6H_2Me_3{\cdot}C(:CH_2){\cdot}O{\cdot}MgX + H^+$ [gives RH]. If the COMe is replaced by CO·OR, in which R is a resonating alkyl group, the R may be ejected in the same way as the H above. Thus, *allyl* iso*durylate* (prep. from the Na salt and $CH_2{:}CH{\cdot}CH_2Br$ at 130—160°), b.p. 115—117°/1 mm., with MgPhBr [or *o*-$C_6H_4Me{\cdot}MgBr$] in Et_2O gives $CH_2Ph{\cdot}CH{:}CH_2$ (I) (67—70%) [or *o*-$C_6H_4Me{\cdot}CH_2{\cdot}CH{:}CH_2$] and 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CO_2H$ (II) (95%). This reaction occurs only when the normal reaction is hindered; thus, *allyl αα-dimethyl-n-propionate*, b.p. 55—56°/36 mm., with MgPhBr gives $CPh_2Bu^{\gamma}{\cdot}OH$ and $CH_2{:}CH{\cdot}CH_2{\cdot}OBz$ gives $CPh_3{\cdot}OH$ (86%) and a little (I). One *o*-Me has little effect, for *allyl* o-*toluate*, b.p. 148°/45 mm., gives *o*-$C_6H_4Me{\cdot}CPh_2{\cdot}OH$ (68%) and an irresolvable mixture. 84% of (II) is obtained by adding 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}MgBr$ in Et_2O to Et_2O through which CO_2 is passed, yields being lower by normal methods. CH_2Ph β-iso*durylate* (prep. from the Na salt and CH_2PhBr in boiling PhMe), b.p. 175—180°/6—8 mm., is also not cleaved by MgPhBr in Et_2O. R. S. C.

Structure of cantharidin and the synthesis of deoxycantharidin. R. B. Woodward and R. B. Loftfield (*J. Amer. Chem. Soc.*, 1941, **63**, 3167—3171).—Formulation of cantharidin (I) as 3 : 6-epoxy-*cis*-1 : 2-dimethyl*cyclo*hexane-1 : 2-dicarboxylic anhydride (A., 1929, 192) is confirmed by synthesis of deoxycantharidin (II). Condensation of $(:CMe{\cdot}CO)_2O$ (III) and $(CH_2{:}CH)_2$ in C_6H_6 at 190—205° (not at lower temp.) (72 hr.) and hydrolysis of the product by 10% aq. NaOH gives cis-1 : 2-*dimethyl*-Δ^4-cyclo*hexene*-1 : 2-*dicarboxylic acid* (IV), m.p. 202·4° (decomp.), converted by boiling AcCl into the *anhydride* (V), m.p. 99·2—99·6° [1 : 1 additive *compound*, m.p. 64—65°, with (III)], hydrogenated (PtO_2; EtOAc) to *cis*-1 : 2-dimethyl*cyclo*hexane-1 : 2-dicarboxylic anhydride, m.p. 129—129·2° [= (II), prep. of which (m.p. 126—128·5°) from (I) is described]. In boiling H_2O, (II) gives deoxycantharidinic acid, but the reverse transformation is also facile and occurs in H_2O, going to completion if the very volatile (II) can sublime away. With Br–AcOH (IV) gives the *bromo-lactone* (VI), m.p. 198·5—199°. With Br–$CHCl_3$, (V) gives a 4 : 5-*dibromide*, m.p. 179—180°, and 4-*bromo*-cis-1 : 2-*dimethyl*-Δ^4-cyclo*hexene*-1 : 2-*dicarboxylic anhydride*, m.p. 89—90° (indifferent to hot $AgNO_3$–EtOH). The evidence now available indicates that in (I) the O- and anhydride rings are probably on the same side of the *cyclo*hexane ring (*exo*-structure). R. S. C.


(VI.)

Isomerisation of naphthalyl chloride. H. E. French and J. E. Kircher (*J. Amer. Chem. Soc.*, 1941, **63**, 3270—3272).—1 : 8-$C_{10}H_6(COCl)_2$ (I) reacts partly in the cyclic form in the Friedel–Crafts reaction (cf. Mason, A., 1925, i, 33, 34). With $AlCl_3$ and C_6H_6 (1 mol.) it gives 50—60% of 1 : 8-$COPh{\cdot}C_{10}H_6{\cdot}CO_2H$ (II), but in one experiment yielded only 13% of (II) and ~40% of a *compound*, m.p. 235—236°, insol. in alkali. With $AlCl_3$ and an excess of C_6H_6, (I) gives (II) (45%), *αα-diphenyl*-1 : 8-*naphthalide* (20%) m.p. 202—203° (corr.) (adds one MgMeI; no active H), and *substances*, m.p. 226—228° (corr.) (7%) and 238—239° (corr.) (3%). Results with PhMe are similar (cf. *loc. cit.*). The structure of *p*-$C_6H_4Me{\cdot}CO{\cdot}C_{10}H_6{\cdot}CO_2H$-1 : 8 is established by decarboxylation to *p*-$C_6H_4Me{\cdot}CO{\cdot}C_{10}H_7$-α and that of αα-di-*p*-tolyl-1 : 8-naphthalide (yield ~80%), m.p. 235—236° (corr.), by addition of one MgMeI and absence of active H. The naphthalides are also prepared from 1 : 8-$C_{10}H_8(CO)_2O$ and LiAr. R. S. C.

Synthesis of condensed ring systems. V. Dianhydride of a steradiene-6 : 7 : 11 : 12-tetracarboxylic acid. L. W. Butz and L. M. Joshel. **VI. Dianhydrides of a tetradecahydrochrysene-1 : 2 : 7 : 8-tetracarboxylic acid and a homologue with an angular methyl group.** L. M. Joshel, L. W. Butz, and J. Feldman (*J. Amer. Chem. Soc.*, 1941, **63**, 3344—3347, 3348—3349).—V. Δ^1-*cyclo*Pentenyl-Δ^1-*cyclo*hexenylacetylene and $(:CH{\cdot}CO)_2O$ at 100—150° (not 70°) give 15—17% (in one experiment, 25%) of $\Delta^{8(14):9}$-*steradiene*-6 : 7 : 11 : 12-*tetracarboxylic anhydride* (I), m.p. 252—255° (vac.), 243—249° (air), or (+dioxan) 246—250°, with ~40% of amorphous alkali-sol. material. The C-skeleton of (I) is proved by conversion by Pd–C or Pd–C–Ca(OH)$_2$ at 260—340° and later 340—390° into 1 : 2-trimethylenephenanthrene. Boiling EtOH converts (I) into the 11-*carbethoxy*-12-*carboxy*-6 : 7-*dicarboxylic anhydride* (or an isomeride) (53%), m.p. 223—230° (gas) [at 250° gives (I)], and a *Et*$_4$ *steradiene*-6 : 7 : 11 : 12-*tetracarboxylate* (8%), m.p. 234—238°. With N-KOH at room temp., (I) gives the


(I.)

tetracarboxylic acid, m.p. 231—232° (dccomp.), m.p. (+dioxan) 213—214° (decomp.) [Me_4 ester (**II**), m.p. 117·5—120·5°; absorbs Br]. Hydrogenation of (**I**) gives mixtures, but that (PtO_2; AcOH) of (**II**) gives Me_4 $\Delta^{8(9)}$-*sterene*-6 : 7 : 11 : 12-*tetracarboxylate* (**III**), m.p. (from MeOH) 165·4—166°, resolidifies, remelts at 168—174°, or (from $COMe_2$–MeOH) 164·5—170°. The following absorption max. and ε, respectively, in EtOH are recorded : (**I**) 2560 A., 19,000; 1 : 2 : 2*a* : 3 : 4 : 5 : 6 : 7 : 8 : 8*a* : 9 : 10 ; 11 : 12 - *tetradecahydrochrysene*-1 : 2 : 7 : 8- (**IV**; see below) 2570 A., 23,500, the derived 2*a*-*methyltetradecahydrochrysene*-1 : 2 : 7 : 8- (**V**; see below) 2540 A., 24,000, and 1 : 5-dimethylhexahydronaphthalene-3 : 4 : 7 : 8- 2470 A., 22,000, -tetracarboxylic anhydride; (**II**) 2560 A., 22,000; (**III**) <~2200 A., 5000.

VI. Di-Δ^1-*cyclo*hexenylacetylene and $(CH{\cdot}CO)_2O$ at 150° give the *dianhydride* (**IV**) (see above) (27%; 19% pure), m.p. 251—254° (vac.). Δ^1-*cyclo*Hexenyl-2′-methyl-Δ^{1}-*cyclo*hexenylacetylene gives similarly 1·9% of (**V**), m.p. 278—280° (vac.). Pd–C converts (**IV**) at 280—350° or (**V**) at 250—330° into chrysene and [from (**IV**)] a small amount of the *lactone*, m.p. 271·8—272·4°, of 2-hydroxymethylchrysene-1-carboxylic acid. M.p. are corr. R. S. C.

Detoxication. XII. Metabolism of vanillin and vanillic acid in the rabbit. Identification of glucurovanillin and structure of glucurovanillic acid. [Colour reaction for *p*-hydroxy- and *p*-methoxy-benzaldehyde.] H. G. Sammons and R. T. Williams (*Biochem. J.*, 1941, **35**, 1175—1189; cf. A., 1942, III, 334).—In the urine of rabbits fed on vanillin (**I**) or vanillic acid (**II**), (**I**) is determined (after hydrolysis) as 2 : 4-dinitrophenylhydrazone, free (**II**) by OMe (Zeisel), and glucurovanillin as the *β-naphthylhydrazone*, m.p. 179°, $[\alpha]_D^{20}$ −78·9° in MeOH, or 2 : 4-*dinitrophenylhydrazone*, decomp. 200° (shrinking at 150°), $[\alpha]_D^{21}$ −68·2° in dioxan, hydrolysed to (**I**). (**II**) is unaffected by dil. HCl under the conditions used for hydrolysing urine. Methylation (Me_2SO_4) of the crude Ba salt of glucurovanillic acid (**III**) from the urine yields veratric acid, its Me ester, and 2 : 3 : 4-*trimethyl*-o-*methoxy*-p-*carbomethoxyphenyl*-β-d-*glucuronide Me ester*, m.p. 137°, $[\alpha]_D^{23}$ −86·05° in $CHCl_3$, hydrolysed (MeOH–HCl) to Me 2 : 3 : 4-trimethyl-αβ-methylglucuronide. (**III**) is therefore a β-pyranuronoside. *p*-OH- and *p*-OMe-aldehydes in urine give an immediate red colour with naphthoresorcinol and conc. HCl in the cold. A. Li.

Normal and abnormal alkylation of 2-methyl*cyclo*pentyl methyl ketone. G. Wash, B. Shive, and H. L. Lochte (*J. Amer. Chem. Soc.*, 1941, **63**, 2975—2979).—1-Benzoyl-2-methyl*cyclo*pentane (**I**) (prep. from *cyclo*hexane by, successively, AcCl–$AlCl_3$, NaOBr, $SOCl_2$, and C_6H_6–$AlCl_3$), b.p. 281°, with $NaNH_2$ and RI in boiling C_6H_6 gives 1-*benzoyl*-1 : 2-*dimethyl*cyclo*pentane* (49%), b.p. 288° (*oxime*, m.p. 161—162°), 1-*benzoyl*-2-*methyl*-1-*ethyl*- (56%), b.p. 304° (*oxime*, m.p. 115—116°), -1-n-*propyl*- (27%), b.p. 312° (no oxime or semicarbazone), and -1-iso*propyl*- (26%), b.p. 315°, -cyclo*pentane*. The 1-Me and 1-Et derivatives with $NaNH_2$ and a little C_6H_6 or xylene, respectively, at room temp. give 1 : 2-*dimethyl*-, m.p. 98·5—99·5°, and 2-*methyl*-1-*ethyl*-cyclo*pentane*-1-*carboxylamide*, m.p. 84·5—85·5°, respectively, but the 1-Pr compounds are unaffected. The latter with O_3 give poor yields of 2-methyl-1-*n*- (*anilide*, m.p. 141—142°) and -1-*iso*-propyl*cyclo*pentane-1-carboxylic acid (*anilide*, m.p. 115—116°). 2-*Methyl*cyclo*pentanecarboxylanilide* has m.p. 107—108°. In xylene at 110—140° *C*-alkylation is replaced by (*a*) formation of 2-methyl*cyclo*pentanecarboxylamide and *N*-alkylation thereof and (*b*) formation of enol *O*-ethers. In boiling PhMe all three reactions occur. 2-*Methyl*cyclo*propanecarboxyl*-*ethyl*-, m.p. 86—87°, and -iso*propyl*-*amide*, m.p. 87—88°, are thus obtained and are also prepared from the acid chloride. 2-α-*iso*Propoxy-, -*n*-propoxy-, and -ethoxy-benzylidene-1-methyl*cyclo*pentane are obtained as oils and identified by ozonolysis. R. S. C.

Comparison of metallic chlorides as catalysts for the Friedel–Crafts ketone synthesis. O. C. Dermer, D. M. Wilson, F. M. Johnson, and V. H. Dermer (*J. Amer. Chem. Soc.*, 1941, **63**, 2881—2883).—Relative efficiencies for prep. of *p*-$C_6H_4Me{\cdot}COMe$ from PhMe and AcCl under optimum conditions are $AlCl_3$ > $SbCl_5$ > $FeCl_3$ > $TeCl_2$ > $SnCl_4$ > $TiCl_4$ > $TeCl_4$ > $BiCl_3$ > $ZnCl_2$. 28 other salts have no catalytic power at the b.p. of PhMe. In many cases >1 mol. of catalyst is required for max. yields, *e.g.*, 3 mols. of $TiCl_4$. Yields often decrease after too long contact, *e.g.*, with $SbCl_5$ and $AlCl_3$ activated by HCl (not pure $AlCl_3$). $PbCl_4$ has slight catalytic effect but causes mainly chlorination; this is also the main reaction if $SbCl_5$ is added first to the PhMe and the yield of ketone is then 2% as against a max. possible ~67%. R. S. C.

Lignin and related compounds. LV. Synthesis and properties of β-hydroxypropioveratrone. LVI. Stability of lignin building units and ethanol-lignin fractions towards ethanolic hydrogen chloride. K. A. West, W. L. Hawkins, and H. Hibbert. **LX. Hydrogenation of maple ethanolysis products. I.** L. M. Cooke, J. L. McCarthy, and H. Hibbert (*J. Amer. Chem. Soc.*, 1941, **63**, 3035—3038, 3038—3041, 3052—3056; cf. A., 1942, II, 42).—LV. 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}CO{\cdot}[CH_2]_2{\cdot}Cl$ (**I**) with Ag_2O in boiling H_2O gives *β-hydroxypropioveratrone* (**II**) (50%), m.p. 83—84°, converted by 4% KOH–MeOH at room temp. (20% yield) or boiling 2% HCl–MeOH (75% yield) into *β-methoxy*- (**III**), m.p. 70—71°, by boiling 2% HCl–EtOH into *β*-ethoxy- (**IV**) (96%), m.p. 50—51° (cf. A., 1939, II, 172), and by AcCl in C_5H_5N–C_6H_6 at 0° (90% yield) into *β-acetoxypropioveratrone* (**V**), m.p. 100—101°. With KOAc–AcOH at 100°, (**I**) gives 70% of (**V**), which with ~3% KOH–MeOH or –EtOH at room temp. gives (**III**) (90%) or (**IV**) (10%), respectively, and with Na_2CO_3 in aq. dioxan at room temp. gives *αβ-epoxypropioveratrone* (60%), m.p. 93—94° (2 : 4-*dinitrophenylhydrazone*, m.p. 182—183°) [not reconvertible into (**V**)]. 72% H_2SO_4 at room temp. converts (**II**) into a lignin-like material. Conversion of (**II**) into (**IV**) under the conditions of ethanolysis of lignin renders it improbable that substances such as (**II**) occur as free lignin-building units in wood.

LVI. Under the conditions of ethanolysis of lignin (boiling 2% HCl–EtOH–CO_2), α-hydroxy- or α-acetoxy-propiovanillone or -propiosyringone is converted into the corresponding α-OEt-ketone but the derived diketones are substantially unaffected. Admixture of OH-ketone and diketone does not affect the result. In all cases some resinification occurs, the amount increasing with rise in concn. of the ketone and being greater in the syringone than in the vanillone series. Interconversion of OH-ketone and diketone during ethanolysis of lignin is thus excluded and these two types must have different origins. Three maple EtOH-lignins are converted by boiling 2% HCl–EtOH into low-boiling oils and products of increased complexity (η), the extent of the conversion decreasing as the complexity of the lignin increases. Thus, the very complex polymerised-condensation products formed during ethanolysis of wood may be derived from less complex polymerides or from monomeric compounds initially present.

LX. With H_2–Cu chromite in dioxan at 250°/3000 lb., 4 : 3 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CO{\cdot}CHMe{\cdot}OEt$ gives 4-*n*-propyl*cyclo*hexanol (**VI**) and much H_2O with small amounts of MeOH and EtOH. Reaction proceeds by hydrogenolysis of OMe (and OEt) to OH + CH_4 (and C_2H_6), hydrogenolysis of the new OH, and reduction of CO to CH_2. That the yield of (**VI**) is only 78% may be due to hydrogenolysis of C·C linkings. The 4-*n*-propyl*cyclo*hexane-1 : 2-diol obtained by hydrogenolysis of MeOH-lignin from aspen (Harris *et al.*, A., 1938, II, 332) may be derived from syringyl components. Hydrogenation, as above, of 4-γ-hydroxy-*n*-propyl*cyclo*hexanol (**VII**) gives ~60% of (**VI**), so that the amount of γ-OH-compounds existing in lignin may exceed the small figure indicated by the yield of (**VII**) obtained from lignin (Harris *et al.*, *loc. cit.*). (**VII**) is identified by oxidation (improved to give 50% yield) to β-4-keto*cyclo*hexylpropionic acid, m.p. 62—64° (*semicarbazone*, m.p. 201—202°). *p*-$OMe{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}CO_2Et$ and HI at 95° give *p*-$OH{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}CO_2H$ (93%), m.p. 127—128°, the Et ester of which is hydrogenated (Raney Ni; EtOH; 210°/200 atm.) to Et β-4-hydroxy*cyclo*hexylpropionate, b.p. 114°/0·6 mm. R. S. C.

***cis–trans* Isomerides derived from 3 : 3-diphenyl-1-hydrindone. Synthesis of 3 : 3-diphenylhydrindene and its derivatives.** P. E. Gagnon and L. P. Charette (*Canad. J. Res.*, 1941, **19**, **B**, 275—290).—3 : 3-Diphenyl-1-hydrindone with ArCHO in MeOH–KOH gives the *trans*-isomeride only, which is converted into the *cis*-isomeride by boiling AcOH, with the exception of *o*-$OEt{\cdot}C_6H_4{\cdot}CHO$, where the *cis*-compound is obtained. The following are described : trans-3 : 3-*diphenyl*-2-o-*methyl*-, m.p. 190° (cis-*compound*, m.p. 176°), -m-*methyl*-, m.p. 175° (cis-*compound*, m.p. 104°), -o-*methoxy*-, m.p. 216° (cis-*compound*, m.p. 182°), -p-*methoxy*-, m.p. 163° (cis-*compound*, m.p. 133°), -o-*ethoxy*-, m.p. 161° (cis-*compound*, m.p. 153°), -o-*chloro*-, m.p. 197° (cis-*compound*, m.p. 151°), and -p-*chlorobenzylidene*-1-*hydrindone*, m.p. 201° (cis-*compound*, m.p. 176°). Reduction (Clemmensen) then affords 3 : 3-*diphenyl*-2-o-, m.p. 132°, and -m-*methyl*-, m.p. 149°, -o-, m.p. 176°, and -p-*methoxy*-, m.p. 178°, -o-*ethoxy*-, m.p. 170°, and -o-, m.p. 160°, and -p-*chloro-benzylhydrindene*, m.p. 156°. 3 : 3-*Diphenyl*-2-*benzylhydrindene* has m.p. 179°. F. R. S.

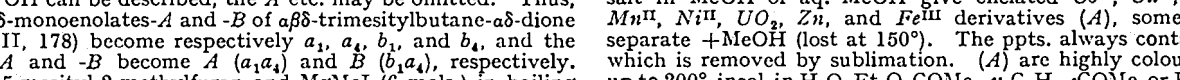
Acylation of the di-enolate of αδ-dimesitylbutane-αδ-dione. R. E. Lutz, W. G. Reveley, and V. R. Mattox (*J. Amer. Chem. Soc.*, 1941, **63**, 3171—3174).—*trans*-αδ-Dimesityl-Δ$^{\beta}$-butene-αδ-dione (**I**) with H_2–PtO_2 in Ac_2O containing $ZnCl_2$ and HCl gives *αδ-diacetoxy-αδ-dimesityl-*Δ$^{\alpha\gamma}$*-butadiene*, dimorphic, m.p. 172° and 162·5° (unaffected by light in I–$CHCl_3$), which with MgMel shows 0·18 active H, adds 3·3 MgMeI, and gives αδ-dimesityl-*n*-butane-αδ-dione (**II**). The *cis*-isomeride of (**I**) resists hydrogenation, but gives under the above conditions 70—75% of 3-acetoxy-2 : 5-dimesitylfuran. Direct acylation of (**II**) failed, but with MgMel (MgPhBr) in Et_2O–N_2 (**II**) gives the dienolate, converted by AcCl into MgI·O·CX:CH·CH(COMe)·COX (X = mesityl), which spontaneously yields 3-*mesitoyl*-5-*mesityl*-2-*methylfuran* (**III**), m.p. 204°, and a little ? *β-acetyl-α-acetoxy-αδ-dimesityl-*Δ$^{\alpha}$*-buten-δ-one* (**IV**), m.p. 193°. In boiling 0·1N-NaOH–EtOH, (**IV**) gives the *enol*, m.p. 109—110° (red $FeCl_3$ colour), of β-acetyl-αδ-dimesitylbutane-αδ-dione, converted by Ac_2O–H_2SO_4 (drop) into (**III**). (**III**) is oxidised by HNO_3 to an enol, whence it is regenerated by Zn dust in boiling AcOH. The dienolate of (**II**) with BzCl–C_6H_6–*iso*amyl ether gives *dibenzoates*, m.p. 186·5° [hydrolysed to (**II**) by alkali] and 181° (hydrolysis leads to resins), respectively. *O*-Acetylation of (**II**) does not occur. R. S. C.

Acylation of the di-enolate of β-phenyl-αδ-dimesitylbutane-αδ-dione. R. E. Lutz and W. G. Reveley (*J. Amer. Chem. Soc.*, 1941,

63, 3175—3178).—MgPhBr and (:CH·COMes)$_2$ (Mes = mesityl here and below) give a dienolate (**I**), MgBr·O·CMes:CH·CPh:CMes·O·MgBr, also formed from COMes·CH$_2$·CHPh·COMes and MgMeI. (**I**) is obtained similarly, but less well, from MgPhBr and (CHBr·COMes)$_2$. With AcCl in Et$_2$O–N$_2$ at >0°, (**I**) gives *βγ-diacetyl-β-phenyl-αδ-dimesityl-*n*-butane-αδ-dione enol acetate* (**II**), OAc·CMe:C(COMes)·CPhAc·COMes or OAc·CMes:CAc·CPhAc·COMes, m.p. 182°. With MgMeI at 100°, (**II**) gives 1 CH$_4$; in HCl–AcOH, (**II**) gives *βγ-diacetyl-β-phenyl-αδ-dimesityl-*n*-butan-αδ-dione enol* (**III**), m.p. 181·5° (with MgMeI gives 1 CH$_4$), converted by Ac_2O containing a little H_2SO_4 at room temp. into a *compound*, $C_{32}H_{32}O_6S$, m.p. 214·5°, and not acetylated by any reagents. Boiling NaOH–EtOH causes *C*-deacetylation of (**II**) or (**III**), yielding 3-*mesitoyl*-4-*phenyl*-5-*mesityl*-2-*methylfuran* (**IV**), m.p. 113° (proof of structure: following abstract). Aq. 25% NaOH and (**II**) give (**IV**) and (probably) *β-hydroxy-γ-phenyl-αδ-dimesityl-*Δ^{β}*-butene-αδ-dione*, m.p. 162·5°. R. S. C.

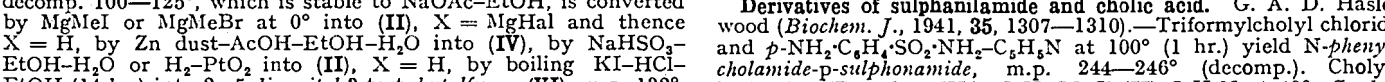
1 : 4-Addition of magnesium methyl iodide to an αδ-unsaturated ketone system involving the ethylenic linking of a 2-aroylfuran, and ring-cleavage of the resulting vinyl allyl ether system. R. E. Lutz and W. G. Reveley (*J. Amer. Chem. Soc.*, 1941, **63**, 3178—3180).—3-Mesitoyl-4-phenyl-5-mesityl-2-methylfuran with MgMeI–Et$_2$O at room temp. (20 min.) and later in boiling Pr$^{\beta}_2$O–N$_2$ gives the dienolate (**I**), MgI·O·CMes:CPh·CBu$^{\gamma}$:CMes·O·MgI (Mes = mesityl), hydrolysed to *β-phenyl-αδ-dimesityl-γ-*tert.*-butyl-*n*-butane-αδ-dione* (**II**), m.p. 164·5°. Longer interaction in Et$_2$O alone gives, after hydrolysis, a compound, decomp. 125°, m.p. 176° (vac.). (**II**) is also obtained from COMes·CH:CBu$^{\gamma}$·COMes (**III**) and MgPhBr, but COMes·CH:CPh·COMes and MgBu$^{\gamma}$Cl give only COMes·CH$_2$·CHPh·COMes. With MgMeI, (**II**) generates 1 CH$_4$ rapidly at room temp. and a second slowly at 100°. Treatment of (**I**) with I– or Br–EtOH at −10° to 0° gives *β-phenyl-αδ-dimesityl-γ-*tert.*-butyl-*Δ^{β}*-butene-αδ-dione*, m.p. 183°, which is also obtained from (**III**) by MgPhBr followed by EtOH–Br at −10° and with H$_2$–PtO$_2$ in EtOH–piperidine gives (**II**). R. S. C.

Stereochemistry of the enols and dienols of αδ-dimesityl-β-tert.-butylbutane-αδ-dione. Proof of 1 : 4-reduction of an α-bromoketone. R. E. Lutz and W. G. Reveley (*J. Amer. Chem. Soc.*, 1941, **63**, 3180—3189).—Structures assigned below (discussed in detail) are proved by the reactions described. Isomeric monoenols are differentiated by letters *a* or *b*, and the position of the OH in the C$_4$-chain by numerals 1—4 (= *α*—δ), *e.g.*, a_1, b_4, etc. Dienols are differentiated as *A*, *B*, etc., the structure and position of the individual OH being added (when known) in parentheses, *e.g.*, *A* (a_4); when both OH can be described, the *A* etc. may be omitted. Thus, the α- and δ-monoenolates-*A* and -*B* of *αβδ*-trimesitylbutane-αδ-dione (A., 1940, II, 178) become respectively a_1, a_4, b_1, and b_4, and the dienolates-*A* and -*B* become *A* (a_1a_4) and *B* (b_1a_4), respectively. 3-Mesitoyl-5-mesityl-2-methylfuran and MgMeI (6 mols.) in boiling Et$_2$O–Pr$^{\beta}_2$O–N$_2$ give the dienolate-*A* (a_4) (**I**; Mes = mesityl, here and below), hydrolysed by dil. HCl to *αδ-dimesityl-β-*tert.*-butylbutane-αγ-dione enol*-a_4 [-Δ^{γ}*-buten-δ-ol-α-one*] (**II**; X = H), m.p. 197° (vac.). (:CH·COMes)$_2$ (**III**) and MgBu$^{\gamma}$Cl (5 mols.) at room temp. to −10° give a mixture of dienol and monoenolate-a_4 [(**II**), X =

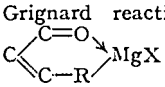
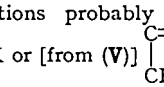


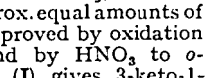
(**I.**) (**II.**)

MgCl]. (**II**), X = H, and unaffected by CH_2N_2 or $FeCl_3$, yields 1 CH$_4$ with MgMeI at room temp. and is then regenerated by hydrolysis, and is converted by hot 2% KOH–MeOH into *αδ-dimesityl-β-*tert.*-butylbutane-αδ-dione* (**IV**), m.p. 112° (with MgMeI liberates 1 CH$_4$ rapidly and a second slowly). With Br–EtOH, (**II**), X = MgI, at −10° gives *γ-bromo-αδ-dimesityl-β-*tert.*-butylbutane-αδ-dione* (**V**), decomp. 100—125°, which is stable to NaOAc–EtOH, is converted by MgMeI or MgMeBr at 0° into (**II**), X = MgHal and thence X = H, by Zn dust–AcOH–EtOH–H$_2$O into (**IV**), by $NaHSO_3$–EtOH–H$_2$O or H$_2$–PtO$_2$ into (**II**), X = H, by boiling KI–HCl–EtOH (14 hr.) into 2 : 5-*dimesityl*-3-tert.*-butylfuran* (**VI**), m.p. 132°, by boiling Ac_2O-containing a little H_2SO_4 into 4-*bromo*-2 : 5-*dimesityl*-3-tert.*-butylfuran*, m.p. 189° [also obtained from (**VI**) by Br–CHCl$_3$], and by boiling KOH–EtOH into *αδ-dimesityl-β-*tert.*-butyl-*Δ^{β}*-butene-αδ-dione* (**VII**), m.p. 115° [reduced to (**VI**) by Zn dust in AcOH]. (**VI**) is also obtained from (**IV**) by boiling HCl–AcOH. The dienolate-*B* (a_4) (**VIII**) is obtained from (**II**), X =



(**VIII.**) (**IX.**) (**X.**)

MgHal, by MgMeI or MgMeBr, and characterised by alkaline hydrolysis to (**IV**), oxidation by I to (**VII**), and acid hydrolysis to (**VI**). The monoenolate-b_4 (? **IX**) is obtained from (**IV**) by MgMeHal and is reconverted into (**IV**) by hydrolysis. With MgMeI in boiling Pr$^{\beta}_2$O, (**IX**) gives the dienolate-*C* (b_4) (**X**), which in I–EtOH gives (**VII**) and (**VI**), and with H_2O_2, KOH–EtOH, or aq. HCl gives (**IV**). Grignard reactions probably proceed by way of complexes,  or [from (**V**)]  , which determine the steric course of the reactions. R. S. C.

Reaction between cyclic β-diketones and Grignard reagents. 1 : 3-Diketo-2 : 2-dimethylhydrindene. T. A. Geissman and V. Tulagin (*J. Amer. Chem. Soc.*, 1941, **63**, 3352—3356).—1 : 3-Diketo-2 : 2-dimethylhydrindene (1 mol.) with 0·25 mol. of MgPhBr in C$_6$H$_6$–Et$_2$O gives 75% of 1-*hydroxy*-3-*keto*-1-*phenyl*- (**I**), m.p. 141—142°, and with 3 mols. of MgPhBr gives 86% of 1 : 3-*dihydroxy*-1 : 3-*diphenyl*- (**II**), m.p. 141—142° [mixed with (**I**), 115—125°], -2 : 2-*dimethylhydrindene*; equimol. proportions give approx. equal amounts of (**I**) and (**II**). The structures of (**I**) and (**II**) are proved by oxidation by $K_2Cr_2O_7$–AcOH to *o*-COPh·C$_6$H$_4$·CO$_2$H and by HNO_3 to *o*-C$_6$H$_4$(COPh)$_2$, respectively. With HCl–ROH, (**I**) gives 3-keto-1-methoxy- (**III**), m.p. 160—162°, and 3-*keto*-1-*ethoxy*-, m.p. 135—136° -1-*phenyl*-2 : 2-*dimethylhydrindene*. MgPhBr in C$_6$H$_6$ converts (**III**) into the Me$_2$ ether (**IV**), m.p. 171·0—171·3° (lit. 172—174°), of (**II**). With MeOH–HCl, (**II**) or (**IV**) gives a Cl-compound, m.p. 172—174° (decomp.), which in boiling MeOH gives 1 : 3-*epoxy*-1 : 3-*diphenyl*-2 : 2-*dimethylhydrindene* (**V**), m.p. 70°. With HCl–CaCl$_2$ in C$_6$H$_6$, (**II**) gives 1 : 3-*dichloro*-1 : 3-*diphenyl*-2 : 2-*dimethylhydrindene*, m.p. 177—178°, converted into (**V**) by boiling MeOH. Attempts to effect cleavage of (**I**) by MgPhBr (to give *o*-COPr$^{\beta}$·C$_6$H$_4$·CPh$_2$·OH) failed. The mechanism of cleavage of 1 : 3-diketones by Grignard reagents is discussed; such cleavage is held to necessitate formation of an intermediate,  . R. S. C.

Preparation of 2-methyl-3-*n*-hexadecyl-1 : 4-naphthaquinone. M. Tishler and N. L. Wendler (*J. Amer. Chem. Soc.*, 1941, **63**, 3235—3236).—2-Methyl-5 : 6 : 7 : 8-tetrahydronaphthalene, C$_{15}$H$_{31}$·COCl, and AlCl$_3$ in CS$_2$ give 3-n-*hexadecoyl*-2-*methyl*-, m.p. 53—55°, reduced (Clemmensen) to 2-*methyl*-3-n-*hexadecyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 45°. S at 205—220° then gives 2-methyl-3-*n*-hexadecylnaphthalene, m.p. 38—40°, oxidised by CrO_3–AcOH at room temp. and later 60° to 2-*methyl*-3-n-*hexadecyl*-1 : 4-*naphthaquinone*, m.p. 98—98·5° (*quinol diacetate*, m.p. 78—79°). The curative dose (vitamin-*K*; chicks; 18 hr.) is 0·2—0·3 mg. R. S. C.

Preparation and properties of phthiocol inner complexes. B. P. Geyer [with G. McP. Smith] (*J. Amer. Chem. Soc.*, 1941, **63**, 3071—3075).—2-Hydroxy-3-methyl-1 : 4-naphthaquinone (**I**) and a metal salt in MeOH or aq. MeOH give chelated *Co*^{II}, *Cu*^{II}, *Fe*^{II}, *Mg*, *Mn*^{II}, *Ni*^{II}, *UO$_2$*, *Zn*, and *Fe*^{III} derivatives (*A*), some of which separate +MeOH (lost at 150°). The ppts. always contain free (**I**) which is removed by sublimation. (*A*) are highly coloured, stable up to 200°, insol. in H$_2$O, Et$_2$O, COMe$_2$, *n*-C$_5$H$_{11}$·COMe, or PhCl, somewhat sol. in MeOH, Bu$^{\alpha}$OH, or PhNO$_2$, decomposed by HCl, NaOH, or dissolution in dioxan. The colour depends on the chelation but the exact position of the absorption max. (recorded) depends on the metal. Catalytic activity for the luminescence of luminol is evinced by (*A*) in the relative order, Co ≫ Cu > Fe^{II} > Fe^{III} > Ni > Mn, the other derivatives being inactive. Details of this effect are studied mainly with the very active Co derivative. EtOH increases the effect but shortens its duration. An inorg. salt of the metal has no catalytic effect and extinguishes the light due to the organo-metallic complex. R. S. C.

IV.—STEROLS AND STEROID SAPOGENINS.

Preparation of Δ^8-, Δ$^{8(14)}$-, and Δ^{14}-cholestenes.—See A., 1942, II, 137.

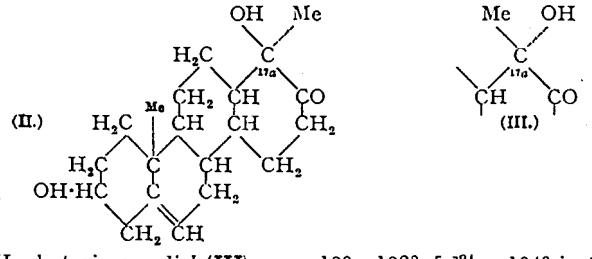
Derivatives of sulphanilamide and cholic acid. G. A. D. Haslewood (*Biochem. J.*, 1941, **35**, 1307—1310).—Triformylcholyl chloride and *p*-NH$_2$·C$_6$H$_4$·SO$_2$·NH$_2$–C$_5$H$_5$N at 100° (1 hr.) yield N-*phenylcholamide*-p-*sulphonamide*, m.p. 244—246° (decomp.). Cholylhydrazine (**I**) and *p*-NHAc·C$_6$H$_4$·SO$_2$Cl (**II**)–C$_5$H$_5$N at 40° afford a product (**III**), decomp. >180° (softens ~160°), hydrolysed by boiling 2N-NaOH to (probably) *α-cholyl-β-*p*-aminobenzenesulphonylhydrazine* (**IV**), m.p. ~150°, decomp. >200°. (**I**), (**III**), or (**IV**) and boiling aq. NaOH give cholic acid, oxidised by CrO_3–AcOH to dehydrocholic acid, also obtained by oxidation of (**III**) or (**IV**). NHBz·NH$_2$ and (**II**) in C$_5$H$_5$N yield *α-benzoyl-β-*p*-acetamido*-, m.p. 219—220° (decomp.), and thence (aq. NaOH) *-amino-benzenesulphonylhydrazine*, m.p. 190—192° (decomp.). A. T. P.

Preparation of unsaturated steroids from steryl sulphates. A. E. Sobel and M. J. Rosen (*J. Amer. Chem. Soc.*, 1941, **63**, 3536—3537).—K cholesteryl sulphate (**I**) with RONa–ROH (R = *n*-C$_6$H$_{13}$·CHMe) at the b.p. (177°) gives 88% of pure Δ$^{3:5}$-cholestadiene, m.p. 79·5—80°, $[\alpha]_D^{26}$ −123·2° in CCl$_4$. In absence of a solvent, (**I**) at 160° or 180° gives impure cholesterylene. With NaOBu$^{\alpha}$–Bu$^{\alpha}$OH at 120°, (**I**) gives the mixed salt, Na(C$_{27}$H$_{45}$)SO$_4$,2K(C$_{27}$H$_{45}$)SO$_4$, m.p. 174—178° (decomp.). With RONa–ROH (R = *n*-C$_6$H$_{13}$·CHMe) at 169°, K cholestanyl sulphate gives the salt, Na(C$_{27}$H$_{47}$)SO$_4$,K(C$_{27}$H$_{47}$)SO$_4$,

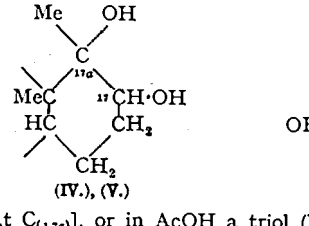
m.p. 234° (decomp.). In absence of NaOAlk hydrolysis is the main reaction. R. S. C.

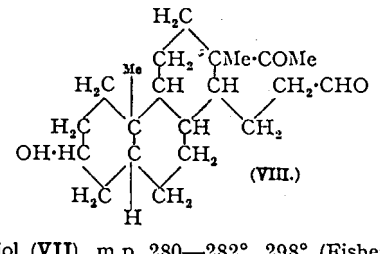
Deoxycorticosterone β-glucoside tetra-acetate.—See A., 1942, II, 134.

Molecular rearrangement of 17-hydroxypregnane compounds. H. E. Stavely (*J. Amer. Chem. Soc.*, 1941, **63**, 3127—3131).—When 17-acetylenyl-Δ^5-androstene-3 : 17-diol is condensed with NH_2Ph in aq. $HgCl_2$ (A., 1940, II, 180), some of the anil is rearranged and resists hydrolysis (even after purification); however, interaction in C_6H_6–H_2O at 60° gives mainly Δ^5-pregnene-3 : 17-diol-20-one (**I**), m.p. 174—176°, $[\alpha]_D^{24}$ −65·5° in $CHCl_3$. Hydrogenation (PtO_2; EtOH) of (**I**) gives *allo*pregnane-3 : 17*α* : 20-triol (*diacetate*, m.p. 166—171°) (with HIO_4 gives, *inter alia*, *iso*androsterone). KOH–EtOH converts (**I**) into Δ^5-*D*-homoandrostene-3 : 17*a*-diol-17-one (**II**). Activated (*i.e.*, alkaline) Al_2O_3 similarly isomerises (**I**) in



C_6H_6, but gives a *diol* (**III**), m.p. 180—182°, $[\alpha]_D^{24}$ −104° in $CHCl_3$ (*acetate*, m.p. 174—176°, $[\alpha]_D^{25}$ −98° in $CHCl_3$), isomeric at $C_{(17\alpha)}$ with (**II**). Oxidation of (**I**) by boiling $Al(OPr^{\beta})_3$–*cyclo*hexanone–PhMe and chromatography (Al_2O_3) of the product gives Δ^4-D-*homoandrosten*-17a-*ol*-3 : 17-*dione* [$C_{(17\alpha)}$ as in (**III**)], m.p. 180°, $[\alpha]_D^{23}$ +60° in $CHCl_3$ (*dioxime*, m.p. 255°), stable to boiling 5% KOH–MeOH, which is also obtained from (**III**) by $Al(OPr^{\beta})_3$–(?)*cyclo*hexanone. Hydrogenation (PtO_2) of (**III**) in EtOH gives D-*homoandrostane*-3 : 17 : 17*a*-*triol* (**IV**), m.p. 259—261° (*mono*-, sinters at 185°, m.p. 190°, and *tri-acetate*, m.p. 247—250°), or in AcOH a *triol* (**V**), m.p. 272—274°, isomeric with (**IV**) only at $C_{(17)}$. Hydrogenation of (**II**) in EtOH gives similarly a *triol* (**VI**), m.p. 256—258° [*di*-, m.p. 220—222°, and *tri-acetate*, m.p. 247°; isomeric with (**IV**)





at $C_{(17\alpha)}$], or in AcOH a triol (**VII**), m.p. 280—282°, 298° (Fisher–Johns apparatus) (lit. 304°) [isomeric with (**V**) at $C_{(17\alpha)}$]. HIO_4 oxidises (**IV**) in aq. MeOH to the *keto-aldehyde* (**VIII**), m.p. 150—152° (*oxime*, m.p. 188—191°, ? of an aldol condensation product; *semicarbazone*, m.p. 187°), which in boiling 5% KOH–MeOH gives a substance, m.p. 181—187°. HIO_4 does not affect (**VI**). CrO_3 oxidises (**V**) or (**VII**) to the same acid, $C_{21}H_{32}O_4$, m.p. 214—216°, 222—225° (Fisher–Johns apparatus) $\alpha \pm 0°$ (Me ester, m.p. 103—105°) (Ruzicka *et al.*, A., 1939, II, 327). R. S. C.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Complete syntheses of pinocamphone, pinonic acid, and α-pinene. G. Komppa, A. Klami, and A. M. Kuvaja (*Annalen*, 1941, **547**, 185—194).—Successive treatments of verbanone (**I**) with Na and I in Et_2O give a dark brown oil, transformed by NaOH–EtOH into a product which does not afford a cryst. semicarbazone. Gradual addition of Br to (**I**) in $CHCl_3$ gives impure dl-*bromoverbanone*, b.p. 100—115°/3 mm., which regenerates (**I**) when boiled with KOH–EtOH. OBr′ and (**I**) do not give a Br-compound. dl-*Chloroverbanone*, obtained by passing Cl_2 through a solution of (**I**) in $CHCl_3$ containing $CaCO_3$, is converted by NaOEt into (**I**) and by NaOBu into a liquid of ill-defined b.p. from which a semicarbazone could not be obtained; when boiled with $NPhMe_2$ or treated with Zn dust it regenerates (**I**). Oximinoverbanone is reduced (H_2–PtO_2–EtOH) to dl-*aminoverbanol*, m.p. 124° [*hydrochloride* (**II**), m.p. 253°; *platinichloride*, m.p. 255° (decomp.); *Ac* derivative, m.p. (anhyd.) 110—114°]; reduction with Zn dust and AcOH gives much less satisfactory results. Treatment of (**II**) with PCl_5 gives a stereoisomeric *amine*, m.p. 111—114° (*hydrochloride*, m.p. 261°). *l*-Verbanone, $[\alpha]_D$ −36·34° (the substance is optically non-homogeneous), is converted by $NaNH_2$ in Et_2O followed by CO_2 into *verbanonecarboxylic acid* (**III**), m.p. 101—102° (decomp.), which loses CO_2 when preserved or, more rapidly, when warmed, and a cryst. *compound*, $C_{10}H_{17}O_3N$, m.p. 170—172°. With NH_2·CO·NH·NH_2 (**III**) affords verbanonesemicarbazone. Reduction of (**III**) at a K–Hg cathode gives *verbanolcarboxylic acid*, m.p. 144—145°. This loses H_2O when heated with Ac_2O, giving d-δ-*pinenecarboxylic acid*, m.p. 123°, $[\alpha]_D$ +10·56° in $CHCl_3$, converted by $SOCl_2$ into the *chloride* (**IV**), b.p. 112—115°/7 mm., and thence (NH_3) into the *amide*, m.p. 142°. Activated $NaNH_2$ in PhMe at 90° and finally at 130° followed by conc. HCl transforms (**IV**) into *l*-pinocamphone (**V**), b.p. 212—214°, $[\alpha]_D$ −11·12° (semicarbazone, m.p. 226—228°). (**V**) is oxidised by aq. $KMnO_4$ to *dl*-pinonic acid (**VI**), m.p. 103° (semicarbazone, m.p. 203—204°). The transformation of (**V**) and (**VI**) into α-pinene has been described by Ruzicka *et al.* (A., 1921, i, 36, 796; 1924, i, 755). H. W.

Camphor, borneol, and allied substances. S. Yamada (*Bull. Chem. Soc. Japan*, 1941, **16**, 239—251).—Catalytic oxidation of borneol (**I**) using one type of reduced Cu catalyst at 400° for 2 hr., or reduced Ni at 300°, affords 96 or 90% of camphor (**II**), respectively; *iso*borneol (**III**) yields similarly, 86 or 89% of (**II**), respectively. Catalytic (reduced Ni) reduction and rearrangement of (**I**), (**II**), and (**III**) at high temp. and pressures are studied; (**II**) is determined by semicarbazone process, and (**I**) and (**III**) are calc. from vals. of $[\alpha]_D$. (**II**) at 140—160°/80 atm. (initial pressure) yields almost equal amounts of (**I**) and (**III**); (**I**) at 170—190°/71 atm. gives only 1% of (**III**), and (**III**) at 130—150°/53 atm. yields 84% of (**I**), with traces of (**II**). Other experiments are carried out in presence of EtOH, AcOH, C_5H_5N, or *cyclo*hexane. αα′-Dimethylcamphor (**IV**) and Na–EtOH give dimethylborneol (**V**), m.p. 57°, $[\alpha]_D^{28}$ +50·72° in EtOH (phenylurethane, m.p. 112—113°; *p*-nitrobenzoate, m.p. 115—115·8°, $[\alpha]_D^{25}$ +50·94° in EtOH; phthalate, m.p. 177—178°, $[\alpha]_D^{27}$ +16·32° in EtOH; Mg phthalate, m.p. 175—176·2°), and dimethyl*iso*borneol (**VI**), m.p. 47—49°, $[\alpha]_D^{15}$ +36·47° in EtOH [phenylurethane, m.p. 116—117°; *p*-nitrobenzoate, m.p. 114·5—115°, $[\alpha]_D^{19}$ +24·9° in EtOH; phthalate, m.p. 173—174° (formed at 110—115°)]. (**IV**) is also reduced by H_2–reduced Ni in presence or absence of AcOH and EtOH, at 220—230°/60 atm., and the amounts of (**V**) and (**VI**) are ascertained; at 280°, some dehydration occurs. A. T. P.

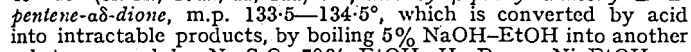
Sapogenins. XII. Position of the carboxyl group in certain triterpene acids. P. Bilham, G. A. R. Kon, and W. C. J. Ross (*J.C.S.*, 1942, 35—42).—Reduction (Clemmensen) of either Me β-boswellenonate or Me β-boswellenedionate gives *Me β-boswellanate*, m.p. 166—167°, $[\alpha]_D$ +131·3° in $CHCl_3$, which could not be saponified. Similar reduction of the Me ester of dihydrobetulonic acid (**I**) affords *Me dihydrobetulanate*, m.p. 166—167°, saponified in very small yield to *dihydrobetulanic acid*, m.p. 293°, more conveniently prepared by reduction of (**I**). The abnormal behaviour of unimol. films of hedraganic acid is not attributable to collapse. Measurements on derivatives of β-boswellic, ursolic, and betulic acid, in which there are no polar groups apart from CO_2H, support the conclusion that in these compounds also the polar group is attached to a terminal ring. The constitution of these triterpenes is discussed. F. R. S.

VI.—HETEROCYCLIC.

Benz*cyclo*octatetraenes. II. Action of acetic anhydride on δ-benzylidenelævulic acids. W. S. Rapson and R. G. Shuttleworth (*J.C.S.*, 1942, 33—35).—δ-Benzylidenelævulic acid and Ac_2O give 2-*keto*-5-*styryl*-2 : 3-*dihydrofuran* (**I**), m.p. 95·5° (cf. Sen and Roy, A., 1930, 1181), which is reduced (Pd–$SrCO_3$–H_2) to 2-*keto*-5-β-*phenylethyltetrahydrofuran*, b.p. 173—175°/7 mm. With the appropriate BzCl derivative (**I**) affords Bz_2, m.p. 177·5—178·5° (lit. 160°), *di*-o-*chloro*-, m.p. 159·5—160°, and *di*-o-*iodo*-*benzoyl* derivatives, m.p. 192—193°. In the OMe series, the following are described: 2-keto-5-*p*-methoxystyryl-2 : 3-dihydrofuran, m.p. 115—115·5° (lit. 78°) (Bz_2 derivative, m.p. 170—171°), and 2-*keto*-5-β-p-*methoxyphenylethyltetrahydrofuran*, b.p. 195—200°/5 mm. F. R. S.

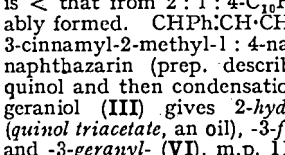
Mechanism of oxidative fission of the furan nucleus. Furans with steric hindrance by one 2-aryl group. R. E. Lutz and W. P. Boyer (*J. Amer. Chem. Soc.*, 1941, **63**, 3189—3192).—*trans*-COMes·CH:CH·CO_2H (Mes = mesityl) [prep. from *s*-$C_6H_3Me_3$, (:CH·CO)$_2$O, and $AlCl_3$ in $(CHCl_2)_2$; 62·5% yield], m.p. 134—137°, with PCl_5 and then $AlCl_3$ in C_6H_6 gives *trans*-COMes·CH:CH·COPh (38—48%), m.p. 60—61°, which does not give the *cis*-isomeride in light, absorbs >1 H_2 (Raney Ni) and after absorption of 1 H_2 gives compounds, m.p. 202·5—203·5° and [? α-*phenyl*-δ-*mesitylbutan*-α(or δ)-*ol*-δ(or α)-*one*], m.p. 86—87°, and with $Na_2S_2O_4$ in boiling 70% EtOH gives α-*phenyl*-δ-*mesitylbutane*-αδ-*dione*, m.p. 52—53°. With warm $SnCl_2$–conc. HCl–AcOH this gives 2-*phenyl*-5-*mesitylfuran*, m.p. 30·5—31°, whence only oils are obtained by HNO_3–AcOH. *p*-C_6H_4Br·CO·CH:CH·COCl, m.p. 100—102°, with *s*-$C_6H_3Mc_3$–$AlCl_3$–$(CHCl_2)_2$ gives trans-α-p-*bromophenyl*-δ-*mesityl*-Δ^{β}-*butene*-αδ-*dione* (79%), m.p. 96—97°, converted by sunlight in C_6H_6 into the cis-*isomeride* (**I**), m.p. 77·5—78°, reduced by $Na_2S_2O_4$–70% EtOH to α-p-*bromophenyl*-δ-*mesitylbutane*-αδ-*dione* (**II**), m.p. 99·5—100°, and reduced and cyclised by $SnCl_2$–conc. HCl–AcOH to 2-p-*bromophenyl*-5-*mesitylfuran* (**III**), m.p. 84° (or, in a preheated bath, 78°, resolidifies, remelts at 84°) [obtained also similarly from (**II**)]. HNO_3–$EtCO_2H$ at −12° to −3° oxidises (**III**) to (**I**). 3-Mesitoyl-4-

phenyl-5-mesityl-2-methylfuran (**IV**) is oxidised by HNO_3–AcOH at 40—45° (cf. A., 1942, II, 144) to *γ-mesitoyl-β-phenyl-α-mesityl-Δ$^{\beta}$-n-pentene-αδ-dione*, m.p. 133·5—134·5°, which is converted by acid into intractable products, by boiling 5% NaOH–EtOH into another substance, and by $Na_2S_2O_4$–70% EtOH, H_2–Raney Ni–EtOH, or $SnCl_2$ into (**IV**). These and previous results indicate that HNO_2-oxidation proceeds by the steps



R. S. C.

Condensation of allylic alcohols with hydroxyquinones. L. F. Fieser and M. D. Gates, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 2948—2953).—2 : 5 : 1 : 4-$(OMe)_2C_6H_2(OH)_2$ [not 1 : 2 : 4 : 5-$C_6H_2(OH)_4$] and phytol (**I**) with anhyd. $H_2C_2O_4$ in dioxan–N_2 at 78° give a mixture, whence 2-*methoxy-5-phytyl*-p-*benzoquinone*, an orange oil, is isolated by chromatography (light petroleum; $MgSO_4$) etc. This gives a pale yellow oily *quinol diacetate* and is formed by elimination of H_2O and MeOH from the primary product. 2 : 1 : 3 : 4-$C_{10}H_4Me(OH)_3$ (**II**), (**I**), and $H_2C_2O_4$ in dioxan at 93° or 81° give similarly vitamin-K_1, identified as quinol diacetate, but the yield is < that from 2 : 1 : 4-$C_{10}H_5Me(OH)_2$ and a mixture is thus probably formed. CHPh:CH·CH_2·OH and (**II**) give similarly the known 3-cinnamyl-2-methyl-1 : 4-naphthaquinone. Reduction of *iso*-naphthazarin (prep. described; 27% yield) by $Na_2S_2O_4$ to the quinol and then condensation as above at 91° with (**I**), farnesol, or geraniol (**III**) gives 2-*hydroxy*-3-*phytyl*- (**IV**), m.p. 56·5—57·7° (*quinol triacetate*, an oil), -3-*farnesyl*- (**V**), an oil (oily *quinol diacetate*), and -3-*geranyl*- (**VI**), m.p. 110—111·5° (*quinol triacetate*, m.p. 111—112·8°), -1 : 4-*naphthazarin*, isolation being tedious. The anti-hæmorrhagic activity of (**IV**) is very great (effective chick dose ~50 μg.) and that of (**VI**) considerable. The structure of (**V**) is proved by its absorption spectrum [max. at 2520 (log *E* 4·26), 2800 (log *E* 4·19), and 3310 A. (log *E* 3·41) in EtOH], which very closely resembles those of lapachol, (**II**), and lomatiol. Cold, conc. H_2SO_4 cyclises (**IV**), (**V**), and (**VI**) to products of β-lapachone type, giving colourless $NaHSO_3$ derivatives: thus are obtained "*β-phytolapachone*" (**VII**), a red oil (nearly colourless *quinol diacetate*), "*β-geranolapachone*," m.p. 232—234° [probably cyclised beyond the stage of (**VII**)], and partly hydrated, impure "*β*-farnesolapachone." 1 : 4 : 5 : 8-$C_{10}H_4(OH)_4$ with (**I**) or (**III**) and $H_2C_2O_4$ as above at 91° give 2-*phytyl*- (**VIII**) and 2-*geranyl-naphthazarin* (**IX**), crimson oils. Et_2O extracts the Na salts of (**IV**), (**VIII**), and (**IX**) completely, mostly, and partly, respectively, from H_2O. M.p. are corr. R. S. C.



(VII.)

Dibenzfuran derivatives.—See B., 1942, II, 57.

Formation of partly acetylated flavone, flavanone, anthraquinone, and similar compounds. V. Simokoriyama (*Bull. Chem. Soc. Japan*, 1941, **16**, 284—291).—The following derivatives are prepared from the respective OH-compound with Ac_2O (5—10 mols.) and 2—3 drops of C_5H_5N: *phloroglucinaldehyde* 2 : 4-*diacetate*, m.p. 93—94°; *gallacetophenone* 3 : 4-*diacetate*, m.p. 78—81°; iso*sakuranetin* 7-*acetate*, m.p. 173—175°, and 5 : 7-*diacetate*, m.p. 138—140° (formed in 5 or 30 min., respectively); *hesperitin* 7 : 3′-*diacetate*, m.p. 103—105°; *chrysin* 7-*acetate*, m.p. 160—165°; *apigenin* 7 : 4′-*diacetate*, m.p. 192—193°; *acacetin* 7-*acetate*, m.p. 203—208°; *baicalein* 6 : 7-*diacetate*, m.p. 194°; *wogonin* 7-*acetate*, m.p. 159—161°; *kæmpferol* 3 : 7 : 4′-*triacetate*, m.p. 177°; *quercetin* 3 : 7 : 3′ : 4′-*tetra-acetate*, m.p. 160—162°; *myricetin* 3 : 7 : 3′ : 4′ : 5′-*penta-acetate*, m.p. 189—190°; *purpurin* 2 : 4-*diacetate*, m.p. 175—178°. A. T. P.

Action of sulphur on hydrocarbons under high pressure.—See A., 1942, II, 125.

Thionaphthen derivatives.—See B., 1942, II, 56.

αβ-Unsaturated amino-ketones. V. Interaction of pyrrolidine and tetrahydroquinoline with bromine derivatives of benzylideneacetophenone. N. H. Cromwell (*J. Amer. Chem. Soc.*, 1941, **63**, 2984—2986; cf. A., 1941, II, 271).—CHPh:CBr·COPh and pyrrolidine (**I**) (not pyrrole) in light petroleum at −10° give *α-bromo-α-pyrrolidino-β-phenylpropiophenone* (**II**), m.p. 106—107° (decomp.; instantaneous), converted by NaOEt–EtOH under reflux into *α-pyrrolidino-β-phenylacrylophenone* (**III**), m.p. 96—98°. CHPhBr·CHBr·COPh with (**I**) gives *αβ-dipyrrolidino-β-phenylpropiophenone*, m.p. 122—123° (hydrolysed slowly in cold 95% EtOH to PhCHO and some $CH_2Ph·CO·COPh$), and some (**III**). Tetrahydroquinoline with (**II**), α-bromo-α-morpholino- or -α-piperidino-β-phenylpropiophenone (0·5 mol.) in EtOH at room temp. gives *α-pyrrolidino-*, m.p. 148—149° (decomp.), *α-morpholino-*, m.p. 153—154°, and *α-piperidino-*, m.p. 166—167° (hydrolysed by 15% H_2SO_4 at 100° to PhCHO and ω-piperidinoacetophenone), *-β-tetrahydroquinolino-β-phenylpropiophenone*. R. S. C.

Reactions of anils. V. Reversibility of the reaction with acid anhydrides. H. R. Snyder and J. C. Robinson, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 3279—3280; cf. A., 1940, II, 87).—Maleanilic acid (**I**) and CHPr$^{\alpha}$:CEt·CHO (**II**) at 100° give 60—70% of 2-phenyl-5 : 7-diethyl-2-aza[2 : 3 : 1]*dicyclo*-Δ^{6}-octen-3-one-8-carboxylic acid (**III**), m.p. 143—144°, also obtained (*loc. cit.*) less well from (:CH·CO)$_2$O and CHPr$^{\alpha}$:CEt·CH:NPh. The 5 : 7-Me_2 analogue, m.p. 157—158°, of (**III**) is similarly prepared by both methods. It is degraded by conc. NaOH to 3 : 5 : 1-$C_6H_2Me_2·CO_2H$. PhNCO decreases the yield of (**III**) from (**I**) and (**II**) but formation of (**III**) in its presence shows that free H_2O is not an essential intermediate in the reaction. (:CH·CO)$_2$NPh does not condense with (**II**) and (**I**) does not react with $(CH_2$:CMe$)_2$. R. S. C.

Heterocyclic derivatives related to sulphanilamide. I. Quinoline analogue of sulphanilamide and [its] derivatives. H. Urist and G. L. Jenkins (*J. Amer. Chem. Soc.*, 1941, **63**, 2943—2944).—Di-5-nitro-8-quinolyl disulphide, m.p. 250—252° (decomp.), and conc. HNO_3 at 100° give *5-nitroquinoline-8-sulphonic acid* (**I**), m.p. >211° (decomp.) (*Na* and *benzyliso*thiocarbamide salt, m.p. 216·5—217·5°), the *amide*, m.p. 186—187°, of which is reduced by Fe powder in 50% AcOH to *5-aminoquinoline-8-sulphonamide*, m.p. 261—265·5° (decomp.). The chloride, m.p. 104—106°, of (**I**) with 2-amino-pyridine or -thiazole in dry C_5H_5N at 0° gives *5-nitroquinoline-8-sulphon-2′-pyridyl-*, m.p. 249—250° (decomp.), and *-2′-thiazyl-amide*, m.p. 260—261° (decomp.), respectively. M.p. are corr. R. S. C.

Syntheses in the quinoline series. II. Derivatives of 4-methylquinoline. Their structure. III. Nitration of 2-chloro-4-methylquinoline. Preparation of 8-dialkylaminoalkylamino-2-hydroxy-4-methylquinolines. O. H. Johnson and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1941, **63**, 2864—2867, 2867—2869; cf. A., 1938, II, 464).—II. 8-Nitro-4-methylquinoline (**I**) (modified prep.) and Raney Ni–H_2 in EtOH at 75°/45 lb. give *8-amino-4-methylquinoline*, m.p. 84°, the diazonium chloride from which with Cu powder in boiling aq. HCl gives *8-chloro-4-methylquinoline* (20%), m.p. 107°, obtained (54% yield) also from 2 : 8-dichloro-4-methylquinoline by Sn–HCl at 80°. With SeO_2 in boiling EtOH, (**I**) gives 53% of 8-nitroquinoline-4-aldehyde, converted by $EtNO_2$ and a little $NHEt_2$ in abs. EtOH at room temp. into *8-nitro-4-β-nitro-α-hydroxy*-n-*propylquinoline* (80%), m.p. 180—190° (decomp.; varies with the rate of heating), which with Raney Ni–H_2 in MeOH at 40 lb. gives *4-amino-4-β-amino-α-hydroxy*-n-*propylquinoline* (51%), m.p. 82—84°. Quinoline-4-aldehyde reacts normally with MgMeI in Et_2O, giving *α-4-quinolylethyl alcohol* (**II**) (55%), m.p. 125° (picrate, m.p. 181°), which is unaffected by HCO_2H at 150°, is reduced to 4-ethylquinoline at higher temp., and is unaffected by 48% HBr at 100°. $SOCl_2$ converts (**II**) in boiling Et_2O into 4-α-chloroethylquinoline (**III**) (picrate, m.p. 180°), which resists the effect of alkali. 2-Hydroxy-4-bromomethylquinoline with boiling NaOMe–MeOH gives *2-hydroxy-4-methoxy-* (78%), m.p. 171° (converted by $POCl_3$ at 130° into *2-chloro-4-methoxy-methylquinoline*, m.p. 64°), with boiling NH_2Ph gives *2-hydroxy-4-anilino-*, amorphous, m.p. 238—240°, and with *p*-OMe·$C_6H_4·NH_2$ in boiling *n*-$C_5H_{11}·OH$ gives *2-hydroxy-4-p-anisidino-*, m.p. 206—207°, *-methylquinoline*. The abnormal properties of (**II**) and (**III**) may be due to existence in "methylene" forms.

III. 2-Chloro-4-methylquinoline and H_2SO_4–HNO_2 (*d* 1·5) at −5° and later room temp. give *2-chloro-8-* (**IV**) (63%), m.p. 135°, and -6-nitro-4-methylquinoline (**V**) (12%), m.p. 212—213° (lit. 207°), the structure of which is proved by conversion into known compounds and by synthesis of (**V**) from 6-nitro-2-hydroxy-4-methylquinoline by boiling $POCl_3$. With Raney Ni–H_2 in MeOH–dioxan at 50°, (**IV**) and (**V**) give *2-chloro-8-* (**VI**), m.p. 102°, and *-6-amino-4-methylquinoline*, m.p. 154°, respectively. 8-Chloro-2-hydroxy-4-methylquinoline (prep. in 12% yield from $CH_2Ac·CO·NH·C_6H_4Cl$-*o* and H_2SO_4 at 65—70°, later 90°), m.p. 212° (lit. 230°), with $POCl_3$ at 135° gives 60% of 2 : 8-dichloro-4-methylquinoline, m.p. 105° (lit. 87—88°), also obtained in 20% yield from (**VI**) by a diazo-reaction. Boiling 80% AcOH hydrolyses (**IV**) to *8-nitro-2-hydroxy-4-methylquinoline* (92%), m.p. 196°, reduced by Raney Ni–H_2 in $COMe_2$ to *8-amino-2-hydroxy-4-methylquinoline*, m.p. >300° (*Ac* derivative, m.p. 252°). With NaOH, MnO_2, and a little Co_2O_3 in boiling MeOH, (**IV**) gives *8-nitro-*, m.p. 119°, reduced to *8-amino-2-methoxy-4-methylquinoline* (**VII**), m.p. 96° which is also obtained from (**VI**) by boiling NaOMe–MeOH Condensation of (**VII**) with Br·$[CH_2]_x·NH_2$,HBr (x = 2 or 3) and NaOAc in boiling EtOH, followed by hydrolysis by boiling 20% HCl gives *8-β-diethylaminoethyl-*, m.p. 140°, and *8-γ-diethylamino*-n-*propyl-amino-2-hydroxy-4-methylquinoline*, m.p. 115°. Quinoline-4-aldehyde hydrate and (**VII**) in boiling abs. EtOH give *8-4′-quinolylmethyleneamino-2-methoxy-4-methylquinoline*, m.p. 144°. R. S. C.

Acid amides as hypnotics. IV. Barbituric acids. F. F. Blicke and M. F. Zienty (*J. Amer. Chem. Soc.*, 1941, **63**, 2991—2993; cf. A., 1942, II, 77).—The following are prepared.
OPh·$[CH_2]_2$·$CH(CO_2Et)_2$, b.p. 215—218°/30 mm.
$CH_2Ph·CEt(CO_2Et)_2$, b.p. 198—203°/32 mm. Et_2 *β*-phenylethyl-ethyl-, b.p. 222—223°/45 mm., *-n-*, b.p. 220—225°/25 mm., and *-iso*-butyl-, b.p. 158—163°/2 mm., *-α′*-phenylethyl-, b.p. 270—275°/58 mm., -malonate. OEt·$[CH_2]_2$·O·$[CH_2]_2$·$CEt(CO_2Et)_2$, b.p. 138—140°/2 mm. $CH_2Ph·C(CH_2·OMe)(CO_2Et)_2$, b.p. 189—192°/14 mm. Et_2 *β*-phenylethyl-methoxymethyl-, b.p. 195—200°/18 mm., -ethoxymethyl-, b.p. 215—218°/23 mm., and *-γ′*-phenoxy-*n*-propyl-, b.p.

298—300°/38 mm., -malonate. Et_2 phenyl-ethoxymethyl-, b.p. 184—187°/14 mm., -butoxymethyl-, b.p. 195—200°/15 mm., -β-methoxyethyl-, b.p. 160—165°/6 mm., and -β-ethoxyethyl-, b.p. 190—193°/14 mm., -malonate. Et_2 β-phenoxyethylethoxymalonate, b.p. 225—230°/29 mm. 5-Benzyl- (*C*), new m.p. 211—212°, 5-α- (*C*), m.p. 207—208°, and 5-β-phenylethyl-, m.p. 168°, 5-γ-phenyl-*n*-propyl-, new m.p. 129—130°, 5-δ-*phenyl*-n-*butyl*-, m.p. 140—141°, 5-ζ-*phenyl*-n-*hexyl*-, m.p. 94—95°, 5-β-cyclo*hexylethyl*-, m.p. 170—171°, 5-*cinnamyl*- (**I**), m.p. 94—95°, 5-methoxymethyl-, new m.p. 185—186°, 5-β-*benzyloxyethyl*-, m.p. 163—164°, 5-β-phenoxyethyl- (*C*), new m.p. 185—186°, and 5-γ-*phenoxy*-n-*propyl*- (**II**), m.p. 123—124°, -5-*ethylbarbituric acid*. 5-β-*Phenylethyl*-5-n-, m.p. 99—100°, and -iso-*propyl*-, m.p. 191—192°, -*allyl*- (*C*), m.p. 151—153°, -n-, m.p. 150—151°, -iso-, m.p. 193—194°, and -sec.-*butyl*-, m.p. 163—164°, -β′-cyclo*hexylethyl*-, m.p. 163—164°, -β′-cyclo*pentylethyl*-, m.p. 166—167°, -α′-*phenylethyl*- (*C*), m.p. 241—242°, -*methoxymethyl*-, m.p. 175—176°, -*ethoxymethyl*-, m.p. 180—181°, -β′-*methoxyethyl*- (*C*), m.p. 164—165°, -β′-*ethoxyethyl*- (*C*), m.p. 169—170°, -β′-*butoxyethyl*-, m.p. 160—161°, -β′-*phenoxyethyl*-, m.p. 210—211°, and -γ′-*propoxy*-n-*propyl*-, m.p. 124—125°, -*barbituric acid*. 5-*Phenyl*-5-*ethoxymethyl*-, m.p. 230—231°, -*butoxymethyl*-, m.p. 182—183°, -β-*methoxyethyl*-, m.p. 210—211°, and -β-*ethoxyethyl*-, m.p. 196—197°, -*barbituric acid*. 5-*Benzyl*-5-*methoxymethylbarbituric acid* (*C*), m.p. 175—176°. 5 : 5-*Di*-β-*phenylethyl*-, m.p. 148—149°, -β-cyclo*hexylethyl*-, m.p. 196—197°, and -γ-*phenoxy*-n-*propyl*-, m.p. 143—144°, -*barbituric acid*. 5-*Ethyl*-5-β′-*methoxy*- (*C*), m.p. 179—180°, -ethoxy- (*C*), new m.p. 179—180°, -*butoxy*- (**III**), m.p. 123—124°, -β′-β″-ethoxyethoxy-, m.p. 96—97°, and -β′-β″-*butoxyethoxy*-, m.p. 83—84°, -*ethylbarbituric acid*. Hypnotic properties of the acids are recorded. The most promising are (**I**), (**II**), and (**III**), which induce very quiet sleep. Compounds marked (*C*) are convulsant.

R. S. C.

Barbiturates containing large radicals. G. S. Skinner and A. P. Stuart (*J. Amer. Chem. Soc.*, 1941, **63**, 2993—2994).—Addition of RBr (1) in $CH_2(CO_2Et)_2$ (1) to $CHNa(CO_2Et)_2$ (1 mol.) in EtOH gives ~85% of Et_2 *n*-do-, b.p. 170—172°/2 mm., *n*-hexa-, b.p. 195—200°/1 mm., and *n*-octa-decylmalonate, b.p. 200—205°/1 mm., converted (method : A., 1937, II, 134) into α-*carbethoxy*-α-n-*dodecyl*-, m.p. 43·5°, b.p. 192—194°/? mm., -*hexadecyl*-, m.p. 49°, b.p. 225—230°/0·3 mm., and -*octadecyl*-, m.p. 55—56°, b.p. 233—238°/0·4 mm., -γ-*butyrolactone*, which, when added with $CO(NH_2)_2$ to NaOEt–EtOH at 10—15° and then gradually heated to 70°, give 81—83% of 5-β-*hydroxyethyl*-5-n-*dodecyl*-, m.p. 145°, -*hexadecyl*-, m.p. 147°, and -*octadecyl*-, m.p. 150°, -*barbituric acid*. Treatment with $CHCl_3$–70% HBr at 50—60° gives 5-β-*bromoethyl*-5-n-*dodecyl*-, m.p. 101·5°, -*hexadecyl*-, m.p. 102·5°, and -*octadecyl*-, m.p. 104·5°, -*barbituric acid*. Hot vapours of the lactones explode in air.

R. S. C.

Pyrimidines. CLXXV. p-Sulphamylanilinopyrimidines. G. de Sütö-Nagy and T. B. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 3234—3235).—*p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ and the appropriate halogenopyrimidine in EtOH give 2 : 6-*di*-p-*sulphamylanilino*-*pyrimidine*, m.p. 280—282°, and -4-*methylpyrimidine*, m.p. 218—220°, 6-p-*sulphamylanilino*-2-, m.p. 239—240°, and 2-p-*sulphamylanilino*-4-, m.p. 237—239°, -*aminopyrimidine*.

R. S. C.

Sulphonamido-derivatives of pyrimidines. J. M. Sprague, L. W. Kissinger, and R. M. Lincoln (*J. Amer. Chem. Soc.*, 1941, **63**, 3028—3030).—M.p. in parentheses below are, successively, those of the *N*-*p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2$ and *N*-*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2$ derivatives (prep. as usual) and are in italics if new. $COMe{\cdot}C_6H_{13}$-*n*, HCO_2Et, and Na in Et_2O give *n*-$C_6H_{13}{\cdot}CO{\cdot}CHNa{\cdot}CHO$, which with guanidine carbonate (**I**) in dry EtOH gives 11% of 2-*amino*-4-n-*hexylpyrimidine* (**II**), m.p. 93—94° (*206—207°*, *214—215°*). $COMePr^{\alpha}$, $COMe_2$, COPhMe, and *cyclo*hexanone give similarly 2-amino-4-*n*-propyl- (**III**) (*217—218°*, *253·5—254°*), -4-mcthyl- (230—231°, 245—246°), -4-phenyl- (*268—269°*, *274—275°*), and -4 : 5-tetrahydrobenz-pyrimidine (252—253°, 255—256°). *n*-$C_6H_{13}{\cdot}CO{\cdot}CH_2{\cdot}CO_2Pr^{\alpha}$ and (**I**) in dry EtOH at 130—150° give 2-*amino*-6-*hydroxy*-4-n-*hexylpyrimidine*, m.p. 199°, converted by $POCl_3$ at 100° into 6-*chloro*-2-*amino*-4-n-*hexylpyrimidine*, m.p. 61—62·5°, which with H_2–Pd–C in EtOH gives (**II**), thus confirming the structure thereof. *n*-$C_5H_{11}{\cdot}CHAc{\cdot}CO_2Et$ and (**I**) at 140—160° give 6-*hydroxy*-2-*amino*-4-*methyl*-5-n-*amylpyrimidine*, m.p. 249—250°, and thence as above 6-*chloro*-2-*amino*-, m.p. 151·5—153°, and 2-*amino*-, m.p. 135—136° (*215—216°*, *182—183°*), -4-*methyl*-5-n-*amylpyrimidine*. $CHEtAc{\cdot}CO_2Et$ gives similarly 2-*amino*-6-*hydroxy*-, m.p. 288—289°, 6-*chloro*-2-*amino*-, m.p. 156—157°, and 2-*amino*-, m.p. 166—167·5°, -5-*ethylpyrimidine*, thus proving the structure of (**III**). $CHBu^{\alpha}(CO_2Et)_2$ gives 2-*amino*-4 : 6-*dihydroxy*-, m.p. 330° (decomp.), and thence 4 : 6-*dichloro*-2-*amino*-, m.p. 170—171°, and 2-*amino*-, m.p. 127—128° (*205—206°*, *241—242°*), -5-n-*butylpyrimidine*. $CHMe(CO_2Et)_2$ gives similarly 2-amino-5-methylpyrimidine (*262—263°*, *271—272°*). 2-*Amino*-4-*ethoxy*-6-*methylpyrimidine*, m.p. 89—90°, 4-*amino*-2-*ethoxypyrimidine*, m.p. 151—152° (*256—257°*, *278—279°*), and 4-*amino*-2-*ethoxy*-6-*methylpyrimidine*, m.p. 109—110° (*186—187°*, *200—201°*), are obtained from the Cl-compounds by NaOEt–EtOH. The following are also described, m.p. in parentheses being those of the N4′-*Ac* derivatives : 2-sulphanilamidopyrimidine, m.p. 251—252° (254—255°); 2-sulphanilamido-4 : 6-dimethyl-, m.p. 175·5—176·5° (240—241·5°), -6-*ethoxy*-4-*methyl*-, m.p. 151—152° (244·5—245°), and -6-*hydroxy*-4-*methyl*-, m.p. 253·5—254°, -*pyrimidine*; 5-*bromo*-2-*sulphanilamido*-4-*methyl*-, m.p. 231—232° (261—262°), 4-*sulphanilamido*-2-*ethylthiol*-6-*methyl*-, m.p. 188—189° (208—209°), 2-*p*-nitrobenzenesulphonamido-4-methyl-, m.p. 230—231°, and 4-p-*nitrobenzenesulphonamido*-2-*ethoxy*-, m.p. 202°, -*pyrimidine*. The above-named sulphonamides are pharmacologically highly active.

R. S. C.

Syntheses in the pyrazine series. IV. 2-Sulphanilamidopyrazine. J. W. Sausville and P. E. Spoerri (*J. Amer. Chem. Soc.*, 1941, **63**, 3153—3154; cf. A., 1940, II, 193).—The prep. of pyrazine-2 : 3-dicarboxylic acid, m.p. (+$2H_2O$) 186° (decomp.), (anhyd.) 190° (decomp.) (first dissociation const. $1{\cdot}7 \pm 0{\cdot}4 \times 10^{-3}$), from quinoxaline is improved (66·8% yield). The 2-carboxylic acid has a first dissociation const. $1{\cdot}2 \pm 0{\cdot}3 \times 10^{-3}$. In boiling $COMe_2$–C_5H_5N 2-aminopyrazine and *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ give 2-*N*⁴-acetylsulphanilamido- (43%), m.p. 240—242°, and thence (hot 6N-HCl) 2-*sulphanilamido*-*pyrazine* (58%), m.p. 251—251·5°.

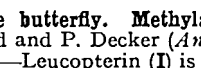
R. S. C.

Indazole derivatives.—See B., 1942, II, 131.

Mechanism and kinetics of ring closure.—See A., 1942, I, 148.

Triazines.—See B., 1942, II, 55.

Ammeline derivatives.—See B., 1942, II, 55.

Wing pigment of the butterfly. Methylation and mol. wt. of leucopterin. H. Wieland and P. Decker (*Annalen*, 1941, **547**, 180—184; cf. A., 1933, 1310).—Leucopterin (**I**) is not attacked by CH_2N_2 in anhyd. Et_2O but addition of about 10% of aq. MeOH causes vigorous evolution of N_2 and production of α- (*anhyd.* and *semihydrate*), m.p. >300°, and β-, m.p. >300°, -*trimethyl-leucopterin*. Determinations of the mol. wt. of these substances in freezing PhOH show that (**I**) is  . Under similar conditions deiminoleucopterin gives an *Me*₄ derivative, m.p. 230°. Passage of Cl_2 through (**I**) suspended in H_2O at 60—70° (cf. *loc. cit.*) yields oxalylguanidine, decomp. 245—260° according to the rate of heating in sealed tubes, m.p. >300° in open tubes, hydrolysed by cautious treatment with 2N-NaOH to $H_2C_2O_4$ and guanidine.

H. W.

Chlorophyll. CV. Chlorination and nitration reaction of porphyrins and chlorins. H. Fischer and W. Klendauer (*Annalen*, 1941, **547**, 123—139).—Gradual addition of 3% H_2O_2 to a solution of pyrroporphyrin in AcOH saturated with HCl gives tetrachloropyrroporphyrin (*dihydrochloride*), also obtained by use of conc. HNO_3 in place of H_2O_2; a slight excess of acid causes total decomp. The salt is transformed by $Cu(OAc)_2$ in boiling MeOH into the *Cu* salt of trichloropyrroporphyrin, m.p. >300°. Reaction with CuCN leads to ill-defined products. Treatment of *pyrroporphyrin Me ester hæmin* with HCl and H_2O_2 leads to a *mono*- and a *di*-*chloropyrroporphyrin Me ester*. Attempts to replace Cl by OH by AgOH, NaOH, etc. lead invariably to pyrroporphyrin, indicating that Cl is probably attached to *tert.* C. Cl_1- and Cl_2-compounds of other porphyrins are obtained by chlorination of the corresponding hæmins, the yield depending greatly on the solubility of the latter in AcOH. It is best to use fresh solutions and to moderate the temp. Protracted action leads to extensive oxidation and decomp. Deuterohæmin yields a well-defined *chlorodeuteroporphyrin ester*, m.p. 215°; there is spectroscopic evidence of a Cl_2-compound. Nitrophylloporphyrin (**I**) is brominated in AcOH at 50° to 6-*bromonitrophylloporphyrin ester*, m.p. 211°, identical with the product obtained by treatment of 6-bromophylloporphyrin with cold HNO_3. The successive action of conc. HNO_3 at room temp. and CH_2N_2 on pyrroporphyrin leads to *nitropyrroporphyrin Me ester*, m.p. 209°; the corresponding *hæmin* has m.p. >300°. Spectroscopic comparison of these compounds with (**I**) shows that NO_2 in (**I**) is not carried by γ-Me. Deuteroporphyrin can be nitrated at room temp. and the product is isolated as *nitrodeuteroporphyrin Me ester*, m.p. 163°. Mesoporphyrin requires somewhat more vigorous treatment for its conversion into *nitromesoporphyrin* Me_2 *ester*, m.p. 165°; it does not give a rhodin under the influence of conc. H_2SO_4–oleum. Unexpectedly rhodoporphyrin is transformed by $NaNO_2$ and AcOH at room temp. followed by CH_2N_2 into *nitrorhodoporphyrin* Me_2 *ester*, m.p. 192° after softening at 285° (complex *Cu* salt, m.p. 220°), which could not be converted catalytically into the corresponding NH_2-derivative. Nitrosation of phæoporphyrin a_5 Me_2 ester appears to yield an NO-compound, hydrolysed by the HCl (used in fractionation) to phæoporphyrin a_7 oxime; this is spontaneously hydrolysed under the experimental conditions so that phæoporphyrin a_7 Me_3 ester is isolated after the treatment with CH_2N_2. Mesochlorin e_6 and conc. HNO_2 yield essentially chloroporphyrin e_5. Under milder conditions ($NaNO_2$–AcOH) the main product appears to be dihydroxymesochlorin e_6, m.p. 115°.

H. W.

Phthalocyanines.—See B., 1942, II, 58.

Oxazolines.—See B., 1942, II, 129.

2-Sulphanilamidothiazoline. G. W. Raiziss and LeR. W. Clemence (*J. Amer. Chem. Soc.*, 1941, **63**, 3124—3126).—Cl·$[CH_2]_3{\cdot}NH_2$,HCl

(prep. in 99% yield from the OH-amine in $CHCl_3$ by HCl gas and later $SOCl_2$) or $Br\cdot[CH_2]_2\cdot NH_2,HBr$ with KCNS gives 2-amino-Δ^2-thiazoline (70%), m.p. 80—82°, which with 1 or 2 mols. of p-$NHAc\cdot C_6H_4\cdot SO_2Cl$ in C_5H_5N–$COMe_2$ at <60° gives 2-N^4-*acetylsulphanilimido*-3-N^4-*acetylsulphanilamidothiazolidine*, m.p. (+H_2O) 164—165° (gas) or (anhyd.) 205—206°. This is hydrolysed by boiling 10% aq. HCl to 2-*sulphanilamidothiazoline* [*sulphathiazoline*] (I) (~50%), shrinks at 207°, m.p. 209—210° (N^4-*Ac* derivative, m.p. 256—258°), 2-sulphanilimido-3-sulphanylthiazolidine, m.p. 259—261° (lit. 265°), and 2-*keto*-3-*sulphamylthiazolidine*, m.p. 206—208°. The effect of (I) against types II and III *Pneumococcus* is equal to that of sulphathiazole but is greater against *Staphylococcus aureus*. R. S. C.

Preparation of 2-amino-4-alkylthiazoles from esters of substituted 2-amino-4-thiazylacetic acids. W. M. Ziegler (*J. Amer. Chem. Soc.*, 1941, **63**, 2946—2948).—Addition of Br to $CHRAc\cdot CO_2Et$ at <20° (subsequent manipulation at >35—40°) gives $CH_2Br\cdot CO\cdot CHR\cdot CO_2Et$, oils, which with $CS(NH_2)_2$ (slightly >1 mol.) and H_2O at 0° give *Et* α-2-*amino*-4-*thiazyl*-n-*butyrate* (I) (42%), m.p. 104—105°, -n-*hexoate* (II) (33%), m.p. 79—80·5°, and -n-*octoate* (III) (45%), m.p. 100—101°. Hydrolysis of (III) by NaOH in hot 95% EtOH gives very rapidly the free *acid* (IV), m.p. ~125° (decomp.), obtained (70%) by acidification of the alkaline solution at 0° but converted by dil. HCl at 50—60° into 2-*amino*-4-n-*heptylthiazole* (V) (85%), b.p. 55—56·5°. 2-*Amino*-4-n-*propyl*- (VI) (78%), m.p. 27—27·5°, and -n-*amyl-thiazole* (VII) (68%), m.p. 45—46°, are similarly obtained from (I) and (II), respectively. p-$NHAc\cdot C_6H_4\cdot SO_2Cl$ does not react with (I), (II), or (III) in $COMe_2$, C_5H_5N at 100°, or quinaldine at 175°, with (IV) in NaOH gives (V), but with (V), (VI), or (VII) gives 2-p-*acetamidobenzenesulphonamido*-4-n-*heptyl*-, m.p. 166—167°, -n-*propyl*-, m.p. 182—183°, and -n-*amyl-thiazole*, m.p. 163—166°. M.p. are corr. R. S. C.

Thiazoles. XXIV. Exchange reactions between 6-nitro-5-alkoxybenzthiazoles and alcohols. H. H. Fox and M. T. Bogert (*J. Amer. Chem. Soc.*, 1941, **63**, 2996—2999; cf. A., 1939, II, 524).—6-Nitro-5-methoxybenzthiazole (I) with KOH–ROH gives 6-*nitro*-5-*ethoxy*- (II), m.p. 156°, -n-, m.p. 130—131°, and -iso-*propoxy*-, m.p. 123·5—124°, -n-*butoxy*-, m.p. 126—127°, -β-*phenylethoxy*-, m.p. 117·5—118°, -β-*hydroxyethoxy*-, m.p. 194—195°, and -cyclo*hexyloxy*-, m.p. 114—115°, -*benzthiazole*. Similarly, 6-nitro-5-methoxy-1-phenyl- gives 6-*nitro*-5-*ethoxy*-1-*phenyl-benzthiazole*, m.p. 158—159°. The reaction is reversible, for (II) with KOH–MeOH regenerates (I). $NH_2\cdot[CH_2]_2\cdot OH$ requires no KOH, for with (I) alone at 100° it gives 6-*nitro*-5-β-*aminoethoxybenzthiazole*, m.p. 206°. With boiling 10% aq. NaOH, (I) or (II) gives 6-*nitro*-5-*hydroxybenzthiazole*, m.p. 156—157° (*K* salt), which could not be alkylated. The lability of the 5-alkoxyl is due to the *vic.* NO_2, since 4-*nitro*-5-*methoxybenzthiazole* [prep. from 2 : 4 : 1-$NO_2\cdot C_6H_3(NH_2)\cdot OMe$], m.p. 184—184·5°, underdoes similar reactions, whereas the 3-NO_2-compound is converted into the disulphide, [2 : 3 : 5 : 1-$NH_2\cdot C_6H_2(NO_2)(OMe)\cdot S]_2$, by rupture of the thiazole ring. M.p. are corr. R. S. C.

5-2′-Thienyl-5-ethylbarbituric acid. F. F. Blicke and M. F. Zienty (*J. Amer. Chem. Soc.*, 1941, **63**, 2945—2946).—Mg 2-thienyl bromide and solid CO_2 in Et_2O–C_6H_6 give thiophen-2-carboxylic acid and thence ($SOCl_2$) the acid chloride, which with CH_2N_2 gives 2-thienyl CHN_2 ketone, m.p. 67—68°, converted by Ag_2O–EtOH into Et 2-thienylacetate (I) (68%), b.p. 124—129°/26 mm. [corresponding Me ester, b.p. 115—118°/23 mm., and acid (II), m.p. 75—76°]. 2-Thienylmethyl chloride and NaCN in EtOH–H_2O give 2-thienylacetonitrile (60%), b.p. 115—120°/22 mm., hydrolysed by KOH–aq. EtOH to (II). Condensation of (I) with $Et_2C_2O_4$ by NaOEt–EtOH at 55° and heating the product with glass powder at 155—160°/20 mm. gives 38% of Et_2 2-thienylmalonate, b.p. 145—148°/5 mm., which with NaOEt–EtBr–EtOH gives Et_2 2-thienylethylmalonate (III) (64%), b.p. 148—150°/5 mm. Condensation of $CO(NH_2)_2$ and (III) by $Mg(OMe)_2$–MeOH gives 5-2′-*thienyl*-5-*ethylbarbituric acid* (58%), m.p. 179—180°, which (as Na salt; rats) has min. lethal and hypnotic doses 200 and 100 mg. per kg. (calc. as acid), respectively. R. S. C.

Thiazole dyes.—See B., 1942, II, 58.

Colour and constitution. II. Absorptions of related vinylene-homologous series. L. G. S. Brooker, F. L. White, G. H. Keyes, C. P. Smyth, and P. F. Oesper. **III. Absorption of 2-*p*-dimethylaminostyrylquinoline and its salts. Effect on absorption of a benzene ring in the chromophoric chain of dyes. IV. Absorption of phenol-blue.** L. G. S. Brooker and R. H. Sprague (*J. Amer. Chem. Soc.*, 1941, **63**, 3192—3203, 3203—3213, 3214—3215; cf. A., 1940, II, 292).—Figures in parentheses below are λ, followed by log ε × 10^4, of the principal absorption max. in MeOH (unless otherwise stated). "Difference" is used for the difference (in A.) between λ of this max. for $X\cdot[CH{:}CH]_n\cdot Y$ and λ of the max. for $X\cdot[CH{:}CH]_{n-1}\cdot Y$. λ of the absorption max. of an unsymmetrical substance, $X\cdot Z\cdot Y$, less the mean λ of the absorption max. of the symmetrical substances, $X\cdot Z\cdot X$ and $Y\cdot Z\cdot Y$, is termed the "deviation" (expressed in A.). μ are dipole moments × 10^{18}. M.p. are corr.

II. For a series, $X\cdot[CH{:}CH]_n\cdot Y$, in which neither X nor Y carries an ionic charge, the "difference" (cf. above) is usually <500 A. and decreases as the series is ascended; thus, λ of the absorption max. increases relatively slowly and blue colours are rare. When X or Y carries an ionic charge, the difference is ~1000 A. even for larger vals. of n and ascent of the series thus soon leads to deep colours. *E.g.*, for cations (I),

(*a*) o-C_6H_4<S / N⁺Et>$C\cdot[CH{:}CH]_n\cdot NHPh$ ⇌

(*b*) o-C_6H_4<S / NEt>$C{:}[CH\cdot CH]_n{:}N^+HPh$, the difference is ~1000 for n = 0—4. For cations (II),

(*a*) o-C_6H_4<S / N⁺Et>$C\cdot[CH{:}CH]_n\cdot NAcPh$ ⇌

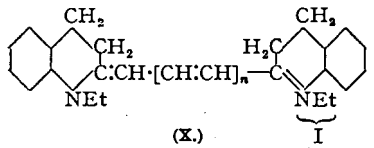
(*b*) o-C_6H_4<S / NEt>$C{:}[CH\cdot CH]_n{:}N^+AcPh$, the difference is 620 (n = 2—1) and 350 for n = 3—2), intermediate between the two above-named types; this is due to the wide difference in basicity of the two N, rendering (II*a*) much more stable than (II*b*), so that resonance is decreased (*i.e.*, the compound is less degenerate). For (I; n = 2), the "deviation" (cf. above) is very small, indicating a degree of resonance approx. equal to that of the symmetrical dyes, *i.e.*, very high. For (I) (n = 0 or 1), the deviation is larger, but not abnormally large. Results for deviations in the series o-C_6H_4<CH₂·CH₂ / N⁺Et>$C\cdot[CH{:}CH]_n\cdot NHPh$ (III) are similar. The lower degeneracy of (II) compared with (I) accounts for (II) being always less deeply coloured than (I) for equal n. Treatment of salts corresponding to (I) with alkali gives (IV),

(*a*) o-C_6H_4<S / NEt>$C{:}[CH\cdot CH]_n{:}NPh$ ⇌

(*b*) o-C_6H_4<S / N⁺Et>$C\cdot[CH{:}CH]_n\cdot N^-Ph$. NHPh is not very acidic, so that (IV*b*) is unstable and degeneracy is low; thus, (IV) are far less deeply coloured than their salts (I). In agreement with these views, deviations for (IV) (n = 0—3) are successively 920, 540, and 370. The existence of (IV*b*) is confirmed by μ greatly exceeding the calc. vals. and by conversion at 100° by p-$C_6H_4Me\cdot SO_3Me$ etc. into salts (V), $\left[o\text{-}C_6H_4\text{<}^{S}_{N^+Et}\text{>}C\cdot[CH{:}CH]_n\cdot NPhMe\right]^{1-}$, the position of the Me in which is proved by synthesis of the tri-iodide corresponding with (V) (n = 3) from $NPhMe\cdot CH[{:}CH\cdot CH{:}]_2NPhMe$]Cl (4490 A.; 8·1) and 1-methylbenzthiazole ethiodide in boiling Ac_2O. In accordance with theory, (i) absorptions of (V) closely resemble those of (I), except that max. are at slightly shorter λ (reason obscure), and deviation is very small, (ii) cations (VI), o-C_6H_4<S / N⁺Et>$C\cdot[CH{:}CH]_n\cdot N<(CH_2)_5$, are highly degenerate, differences (n = 0—3) being ~1000 and absorptions closely resembling those of (V), and (iii) the cation (VII),

o-C_6H_4<S / N⁺Et>$C\cdot[CH{:}CH]_2\cdot NMe_2$, is highly degenerate, absorption resembling that of (VI) (n = 2) and the deviation being very small. Degeneracy leads to stabilisation by resonance and consequently lower reactivity; thus, (II) reacts much faster than the more degenerate (V) or (VI) with 2-methylbenzthiazole ethiodide in boiling C_5H_5N or with 3-phenylrhodanine in boiling abs. EtOH–NEt_3, and (II) reacts faster than (V) with (VI) (elimination of piperidine). The following are prepared. 1-*Phenylthiolbenzthiazole* [from 1-chlorobenzthiazole (1 mol.), PhSH (2), and NEt_3 (2 mols.) at 100°], b.p. 183—187°/3 mm. [*ethiodide* (VIII), m.p. 167—168° (decomp.)]. 1-*Ethylthiolbenzthiazole ethiodide*, m.p. 115—117° (decomp.). 1-*Anilino*- (I) (n = 0) [from (VIII) by NH_2Ph (2 mols.) in boiling EtOH or, better, from 1-anilinobenzthiazole by EtI], cream-coloured, m.p. 197—198° (decomp.) (2985 A., 1·4), 1-β-anilinovinyl- (I) (n = 1) [from (II) (n = 1) and NH_2Ph in boiling EtOH], buff, m.p. 265—266° (decomp.) (4140 A., 5·5), 1-δ-*anilino*-$\Delta^{\alpha\gamma}$-*butadienyl*- (similarly prepared) (I) (n = 2), brown, m.p. 250—252° (decomp.) (5160 A., 10·7), and 1-ζ-anilino-$\Delta^{\alpha\gamma\epsilon}$-hexatrienyl- (I) ($n$ = 3), m.p. 161—163° (decomp.) (6125 A., 7·6), -benzthiazole ethiodide. 1-β-Acetanilidovinyl- (II) (n = 1) [from 1-methylbenzthiazole ethiodide (IX) and $NH{:}CH\cdot NPh_2$ in boiling Ac_2O or from (I) (n = 1) by Ac_2O–C_5H_5N], almost colourless, m.p. 231—233° (decomp.) (3640 A., 1·0), 1-δ-acetanilido-$\Delta^{\alpha\gamma}$-butadienyl- (II) (n = 2) [from (IX) and $NHPh\cdot CH{:}CH\cdot CH{:}NPh,HCl$ in boiling Ac_2O or (I) (n = 2)], brownish, m.p. 233—234° (decomp.) (4260 A., 3·5) (slowly hydrolysed in MeOH), and 1-ζ-*acetanilido*-$\Delta^{\alpha\gamma\epsilon}$-*hexatrienyl*- (II) ($n$ = 3) [from (VIII) and $CH_2(CH_2\cdot CO\cdot NHPh,HCl)_2$ in boiling Ac_2O], reddish-brown, m.p. 203—205° (decomp.) (4610 A., 4·4), -*benzthiazoline ethiodide*. 1-*Anilo*-2-*ethyl*-, colourless, m.p. 64—65° [3020 A., 1·1; μ 2·37±0·03 (calc. 1·6±0·6)], 2-*ethyl*-1-β-*aniloethylidene*-, amber (blue reflex), m.p. 98—99° (decomp.) [3940 A., 3·8; μ 4·17±0·12 (calc. 2·0±0·6)], 2-*ethyl*-1-δ-*anilo*-Δ^{β}-*butenylidene*-, orange-brown, m.p. 109—110° (decomp.) [4480 A., 5·9; μ 5·32±0·10 (calc. 2·0±0·6)], 2-*ethyl*-1-ζ-*anilo*-$\Delta^{\beta\delta}$-*hexadienylidene*-, brown, m.p. 117—119° (decomp.) (4850 A., 6·8), -*benzthiazoline* (IV) (n = 0—3), prepared from the appropriate (I) by NaOH–$COMe_2$–H_2O. 1-N-*Methylanilino*- (V) (n = 0), colourless, m.p. 194—195° (2930 A., 1·3), and 1-δ-*methylanilino*-$\Delta^{\alpha\gamma}$-*butadienyl*- (V) (n = 2), orange-brown (green reflex), m.p. 236—238° (decomp.) (4965 A., 10·7)

[corresponding *tri-iodide*, green, m.p. 194—196° (decomp.)], *-benzthiazole ethoperchlorate*. 1-*β-Methylanilinovinyl-*, yellow, m.p. 213—214° (decomp.) (4000 A., 4·6), and 1-*ζ-methylanilino-*$\Delta^{\alpha\gamma\epsilon}$*-hexatrienyl-*, blue, m.p. 157—158° (decomp.) (5975 A., 13·3), *-benzthiazole ethiodide* (**V**). 1-*Piperidinobenzthiazole ethoperchlorate* (**VI**) (n = 0), colourless, m.p. 129—130° (2950 A., 0·8). 1-*β-Piperidinovinyl-*, cream, m.p. 274—277° (decomp.) (3880 A., 5·1), 1-*δ-piperidino-*$\Delta^{\alpha\gamma}$*-butadienyl-*, red, m.p. 205—207° (decomp.) (4830 A., 14·2), and 1-*ζ-piperidino-*$\Delta^{\alpha\gamma\epsilon}$*-hexatrienyl-*, blue, m.p. 172—175° (decomp.) (5840 A., 21·8), *-benzthiazole ethiodide* (**VI**) (n = 1—3), prepared from (**II**) by piperidine in boiling EtOH. 2-*β-Anilinovinyl-* (prep. from quinaldine ethiodide and $NH{:}CH{\cdot}NPh_2$ at 180°), amber, m.p. 282—285° (decomp.) (4430 A., 5·1), and 2-*δ-anilino-*$\Delta^{\alpha\gamma}$*-buladienyl-* (prepared similarly by $NHPh{\cdot}CH{:}CH{\cdot}CH{:}NPh,HCl$–$Ac_2O$ and later NH_2Ph–EtOH), brown (blue reflex), m.p. 238—240° (decomp.) (5280 A., 9·5) [*Ac* derivative, m.p. 231—234° (decomp.)], *-quinoline ethiodide* (**III**) (n = 1—2). 1-*δ-Dimethylamino-*$\Delta^{\alpha\gamma}$*-butadienylthiazole ethiodide* (**VII**) [prep. as for (**VI**)], red, m.p. 244—246° (decomp.) (4820 A., 13·4).

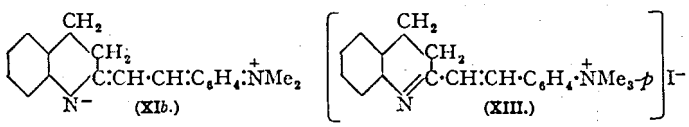


(X.) I

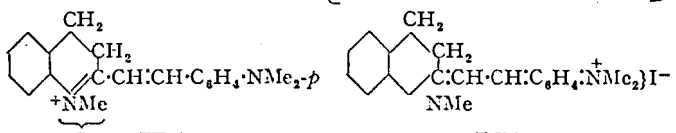
3-Phenyl-5-β-2′-ethyl-1′-benzthiazolinylidenevinylrhodanine, m.p. 283—285° (decomp.).

$o\text{-}C_6H_4\langle$S, NEt$\rangle$C:CH·[CH:CH]$_n$·C$\langle$S, N$^+$Et$\rangle$C$_6$H$_6$-$o\}I^-$, n = 0 (4230 A., 8·45) and 1 (5575 A., 14·8). $\{NHPh{\cdot}CH[{:}CH{\cdot}CH{:}]_nNPh\}X$, n = 1 (3825 A., 5·0) and 2 (4850 A., 6·5). (**X**), n = 0 (5235 A., 7·6) and 1 (6040 A., 19·4). $NMe_2{\cdot}[CH{:}CH]_2{\cdot}CH{:}NMe_2\}ClO_4$ (4130 A., 4·8).

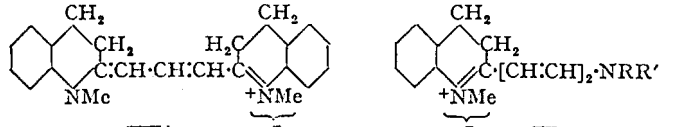
III. The yellow colour of 2-*p*-dimethylaminostyrylquinoline (**XI***a*) (3960 A., 4·02) is due to resonance with the form (**XI***b*). Its red methiodide (Rupe *et al.*, A., 1936, 83) (5520 A., 5·78; in $MeNO_2$



(XI*b*.) (XIII.)



(XII*a*.) (XII*b*.)



(XIV.) I (XVI.)

5260 A., 5·9) owes its colour to the resonance (**XII**; $a \rightleftharpoons b$), and the isomeride (**XIII**) is colourless because resonance is impossible. However, the deviation of (**XII**) is very high (825 A.). This is not due to difference in basicity of the N, for the symmetrical analogues (**XIV**) (6040 A., 18·5; in $MeNO_2$ 6070 A., 13·3) and $[p\text{-}NMe_2{\cdot}C_6H_4{\cdot}CH{:}C_6H_4{:}N^+Me_2]X$ (**XV**) (in $MeNO_2$ 6100 A., 13·1) are blue and have very similar adsorption. Nor is it due to the aminoalkylidene side-chain, for (**XVI**) shows no deviation. It is due to the stability of (**XII***a*) being enhanced by the Kekulé forms of the C_6H_6 ring. This effect is not shown with (**XV**) as the resonance forms are equiv., but is operative in a homologue of (**XII**) [difference from (**XI**) 150 and from (**XII**) 360 A.] and in the benzthiazole series. The very slight degeneracy of (**XI**) is due to three causes: the C_6H_6 effect, the instability of $>N^-$ in the quinoline nucleus of (**XI***b*), and the dipole nature of (**XI**) [μ 3·12 (calc. 2·6)]. The effect of a C_6H_6 ring on resonance is elaborated also for Michler's ketone, phenol-blue, auramine, and malachite-green. The aldehydic character of $p\text{-}NMe_2{\cdot}C_6H_4{\cdot}[CH{:}CH]_n{\cdot}CHO$ and non-aldehydic character of $NMe_2{\cdot}CHO$ is similarly due to the C_6H_4 of the former. A general rule, that the effect on the deviation produced by a change in chemical structure is greater the more degenerate is the compound undergoing change, is postulated and illustrated. Among cyanine dyes in general substitution of 2-quinolyl by 1-benzthiazolyl lessens the colour. This substitution has no effect on very low deviation of the highly degenerate 2 : 2′-carbocyanines, but has an effect on the less degenerate (**XII**). For (**XI**) and its benzthiazole analogue, the lower basicity of benzthiazole renders the (**XI***b*) form more stable and thus reverses the usual effect, deepening the colour; further, replacement of quinoline in (**XI**) by the much less basic 1 : 2-dimethylindole actually leads to a negative deviation (−95 A.; ? interpretation of the negative sign); but for the highly degenerate mixed 2-quinonyl-1-benzthiazolylcarbocyanine the different basicity of the nuclei is without effect and the deviation is negligible. The following are prepared by methods generally similar to those given above. 2-*δ-Anilino-*, brown (blue reflex), m.p. 231—232° (decomp.) (5285 A., 9·50), 2-*δ*-N-*methylanilino-*, dark, m.p. 205—207° (5150 A., 9·9), and 2-*δ-dimethylanilino-*, black (bluish reflex), m.p. 260—261° (decomp.), -$\Delta^{\alpha\gamma}$*-butadienylquinoline methiodide* (**XVI**). 2-*δ-Anilo-*Δ^{β}*-butenylidene-1-methyl-*1 : 2*-dihydroquinoline*, m.p. 101—102°. 2-*δ-p-Dimethylamino-*$\Delta^{\alpha\gamma}$*-butadienylquinoline* (from quinaldine and *p*-$NMe_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CHO$ in conc. HCl at 100°), orange, m.p. 182—184° (decomp.) (4110 A., 4·0) [*methiodide*, green, m.p. 262—264° (decomp.) (5580 A., 4·9)]. 2-p-*Dimethylaminostyrylbenzthiazole*, yellow, m.p. 206—208° (decomp.) [4000 A., 2·81; μ 3·59 (calc. 2·2)] [ethiodide (5240 A., 6·5; in $MeNO_2$ 5280 A., 6·3)]. 1′-*Methyl-*3-*n-propyl-* (prep. from quinaldine metho-*p*-toluenesulphonate and 1-*β*-acetanilidovinylbenzthiazole *n*-propiodide in boiling C_5H_5N), m.p. 255—257° (decomp.) (5790 A.), and 3 : 1′-*diethyl-* (prep. similarly using 1-*β-N*-methyl- or 2-*β*-piperidino-vinylbenzthiazole ethiodide), green, m.p. 276—277° (decomp.) (5780 A., 13·6), and 3 : 3′-diethyl- (in $MeNO_2$ 5565 A., 13·1) -thia-2-carbocyanine iodide. 3-p-*Dimethylaminobenzylidene-2-methylindolenine methoperchlorate*, m.p. 183—185° (decomp.) (in $MeNO_2$ 5530 A., 4·35).

$NPhR{\cdot}[CH{:}CH]_2{\cdot}CH{:}NPhR\}X$, in which R = H (4850 A., 6·5) or Me (4490 A., 8·1). 3-1′ : 2′-Dimethylindolenylmethylene-2-methylindolenine methiodide (in $MeNO_2$ 4900 A., 5·3).

IV. Phenol-blue owes its colour to resonance, (*a*) *p*-$NMe_2{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}O$-*p* $\rightleftharpoons$ (*b*) *p*-$N^+Me_2{\cdot}C_6H_4{\cdot}N{\cdot}C_6H_4{\cdot}O^-$-*p*, and has very high μ (5·80±0·17 in C_6H_6; calc. 2·4±0·5). The stability of (*b*) and thus the depth of colour is greatly dependent on the dielectric const. (ϵ) of the solvent; absorption max. are: in *cyclo*hexane (ϵ 2) (reddish-violet solution) 5520, in $COMe_2$ (ϵ 21) 5820, in MeOH (ϵ 31) 6120, and in H_2O (ϵ 80) (deep blue solution) 6680 A. This effect is not shown by the symmetrical *p*-$NMe_2{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}NMe_2$-*p*}I and *p*-$O{:}C_6H_4{:}N{:}C_6H_4{:}O$-*p*}Na, which have absorption max. 7290—7260 and 6280—6420 A., respectively, in $COMe_2$, MeOH, and H_2O.

R. S. C.

VII.—ALKALOIDS.

Calabash curare. III. H. Wieland, H. J. Pistor, and K. Bähr. **IV.** H. Wieland, K. Bähr, and B. Witkop (*Annalen*, 1941, **547**, 140—155, 156—179; cf. A., 1938, II, 463).—III. The calabash contents are made into a stiff paste with H_2O and extracted with MeOH. The dried extract is dissolved in H_2O and the solution is completely pptd. with Reinecke acid. The dried ppt. is dissolved in 10 parts of $COMe_2$, the insol. brown matter is centrifuged, and the clear solution treated with 5 vols. of hot H_2O. The process is repeated until ~65% of the original material has been removed. The pptd. reineckates are fractionated chromatographically (Al_2O_3) and the individual fractions are converted into hydrochlorides by successive treatments with Ag_2SO_4 and $BaCl_2$. Dissolution of *C*-curarine I hydrochloride (**I**) in conc. HCl leads to an intensely violet solution the colour of which is completely discharged by sufficient dilution with H_2O. A distinct colour results with 20% HCl. (**I**) is chemically unchanged after several hr. but gradually undergoes decomp. The nature of the halochromism remains unexplained. (**I**) if moistened with Et_2O and then dried in a vac. at room temp. has the composition $C_{20}H_{23}ON_2Cl$, but after remaining in a vac. at room temp. until const. in wt. it is $C_{20}H_{21}N_2Cl$. It remains uncertain whether H_2O of crystallisation is present since although the anhyd. salt acquires H_2O when recrystallised the corresponding hydriodide retains its complete H_2O content at 150°/vac. At 100° only a small proportion of the Cl in (**I**) remains in ionic union, the greater part becoming attached firmly to C. The colour reactions of (**I**) are described. (**I**) is transformed by KOH–MeOH at 150° into the ether *base* (**II**), $C_{40}H_{42}ON_4$, m.p. 184°, thus indicating the possible presence of a quinoline or *iso*quinoline ring in (**I**). (**II**) affords a *methiodide*, m.p. 300°, which does not lend itself to the Hofmann degradation. At 200°, (**II**) passes into an isomeric *base*, m.p. >300° after darkening at ~280°. Hydrogenation of (**II**) by Na and boiling $C_5H_{11}{\cdot}OH$ yields the H_4-base (**III**), $C_{40}H_{46}ON_4$, m.p. 105—110° (decomp.) (*methiodide*), also obtained similarly from (**I**), whereas in AcOH containing PtO_2 the product is an *octahydride*, m.p. (indef.) 90—95° after softening at 80° (non-cryst. *methiodide*), also obtained similarly from (**II**). (**I**) is immediately converted by Br–H_2O (1 mol.) into *C-bromocurarine* I *hydrochloride*, characterised by its great toxicity and converted by Ag_2O–$Ba(OH)_2$ into the *brominated ether base*, $C_{40}H_{40}ON_4Br_2$, which is pharmacologically inactive. (**I**) is transformed by HNO_3 (*d* 1·2) into *C-nitrocurarine* I *nitrate*, which is 20 times as toxic as the initial curare base. *C*-Curarine II is most conveniently purified through the *picrate*, m.p. 203—204° (corresponding *perchlorate* and *platinichloride*). The hydrochloride is readily brominated and nitrated. The monosubstituted derivatives are much more toxic than the parent base but a $(NO_2)_2$-base is less active. *C*-Curarine III is best purified through the cryst. *anthraquinonesulphonate*, decomp. 308—310°, which is converted into the hydrochloride, decomp. 270—274°, $[\alpha]_D^{20}$ −936·9° in H_2O (corresponding *picrate*, m.p. 189°). This can also be obtained directly. It has no pharmacological activity.

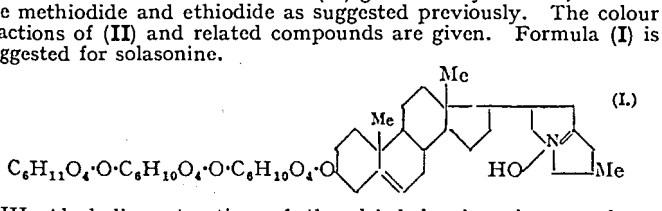
The pptd. reineckates (see above) contain the whole of the biologically active material. The mother-liquors yield curine, m.p. 212° (monohydrate and anhyd.), $[\alpha]_D^{20}$ −328° in C_5H_5N, identical with that described by Boehm.

IV. Application of the modified method of isolation (sec above) to calabashes from Urbana and Caracas leads to the isolation of *C-dihydrotoxiferin* I *hydrochloride* (**IV**), $C_{20}H_{23}N_2Cl$, $[\alpha]_D^{20}$ −610·6° in EtOH, −605° in EtOH–H_2O (1 : 1), which has a more rapid and less prolonged physiological action than (**I**), from which it also differs in the absence of halochromism; the corresponding *sulphate*, *hydrobromide*, darkens above 260°, and *picrate* (+H_2O), m.p. 183—185°, are described. *C*-iso*Dihydrotoxiferin* I is present in many calabashes with *C*-curarine I, which it completely resembles in activity; the *hydrochloride*, $C_{20}H_{23}N_2Cl,3H_2O$, $[\alpha]_D^{20}$ −566° in H_2O, which gives a red-brown colour with conc. HNO_3 and does not exhibit halochromism with conc. HCl, the *perchlorate*, and *picrate*, decomp. 242° after softening at 200°, are described. It yields a NO_2-compound. *C-Toxiferin* II *hydrochloride*, $[\alpha]_D^{20}$ +72·1° in H_2O [corresponding *picrate*, m.p. 215° (decomp.) when rapidly heated], is obtained from calabashes from Urbana and Caracas. If the picrate is decomposed in the usual manner with HCl, the product is the much less physiologically active *toxiferin* IIa *hydrochloride* (**V**), decomp. 275° after becoming brown at 250°, $[\alpha]_D^{20}$ +66·3° in H_2O; the corresponding *picrate* has m.p. 210° (decomp.). Contact with Al_2O_3 transforms this hydrochloride into *toxiferin* IIb *hydrochloride* (**VI**), slow carbonisation at >260° after becoming brown at 240°, $[\alpha]_D^{20}$ +78·4° in H_2O [corresponding *picrate*, m.p. 215° (decomp.)], which has lower pharmacological activity. The isolation of (**I**) from the mother-liquors of (**IV**) is described. *Toxiferin* I hydrochloride, $[\alpha]_D^{20}$ −610° in H_2O, activity 0·5 μg. per frog (corresponding *picrate*, m.p. 270° after darkening), which gives a brownish-green, non-characteristic colour with conc. HNO_3 and does not show halochromism with conc. HCl, *toxiferin* II *picrate*, m.p. 216°, (**V**), and (**VI**) are also derived from *Strychnos toxifera*. The alkaloids from the latter source are therefore present in the calabashes of arrow poison but the residues from the aq. extract of the plant are pharmacologically less active than the prepared poison. Apparently the latter material is obtained from a great variety of plants.

H. W.

Solanum **alkaloids. I. Alkaloid from the fruit of** *S. aviculare*. R. C. Bell and L. H. Briggs. **II. Solasonine.** L. H. Briggs, R. P. Newbold, and N. E. Stage. **III. Alkaloids from** *S. auriculatum*. R. C. Bell, L. H. Briggs, and J. J. Carroll. **IV. Glycosidic moiety of solauricine.** L. H. Briggs and J. J. Carroll (*J.C.S.*, 1942, 1—2, 3—12, 12—16, 17—18).—I. The alkaloid, previously regarded as purapurine, is solasonine (**I**).

II. Analyses support formulæ $C_{45}H_{73}O_{16}N$ for (**I**) (from *S. sodomæum*) and $C_{27}H_{43}O_2N$ for solasodine (**II**), and lead to the formulation of (**I**) as a trisaccharide containing rhamnose, galactose, and glucose units with one mol. of (**II**) (cf. Oddo *et al.*, A., 1936, 488). (**II**) contains the steroid nucleus and has one OH in a *cis*-position at $C_{(3)}$ and a double bond at $C_{(5)}$–$C_{(6)}$. It forms an Ac derivative sol. in acids, give *dihydrosolasodine*, m.p. 208·5—210·5°, $[\alpha]_D^{25}$ −63·5° in $CHCl_3$, on catalytic hydrogenation (Pd–C), and with Br–$CHCl_3$ or Br–AcOH followed by crystallisation from H_2O–EtOH–$COMe_2$–HBr gives a *hydrobromide*, $C_{27}H_{43}O_2NBr,HBr$, m.p. 302° (decomp.). Dehydration with HCl–EtOH affords $\Delta^{3:5}$-solasodiene, which is hydrogenated (PtO_2–H_2) to *hexahydrosolasodiene* (*dihydro*chano*solasodan*), m.p. 184—186°, $[\alpha]^{25}$ −18° in $CHCl_3$, formed by saturation of the normal double bonds and further by opening up of the heterocyclic rings. Similar hydrogenation of (**II**) gives tetrahydrosolasodine (dihydro*chano*solasodanol). HNO_2 and (**II**) yield a quaternary *nitrite*, m.p. 260·5—262·5° (decomp.), the " azosolasodine " of Oddo. MeI or EtI with (**II**) gives the hydriodide, and not the methiodide and ethiodide as suggested previously. The colour reactions of (**II**) and related compounds are given. Formula (**I**) is suggested for solasonine.



(I.)

III. Alcoholic extraction of the dried berries gives a glycoalkaloid, *solauricine* (**III**), $C_{45}H_{73}O_{16}N$, m.p. 269·5—270° (decomp.), hydrolysed to a mixture of sugars and *solauricidine* (**IV**), $C_{27}H_{43}O_2N$, m.p. 220—223°, $[\alpha]_D^{25}$ −89·8° in MeOH [*hydrochloride* (+$2H_2O$), $[\alpha]_D^{25}$ −68·2° in MeOH; *sulphate* (+0·5H_2O); *hydriodide*; *picrate* (+H_2O); and *nitrite*]. Evidence is adduced that (**IV**) is neither identical with nor a dimorphic form of (**II**) but is extremely closely related to it physically and chemically; no structural differences have yet been found. From the juice of the green berries, a product, m.p. 269—270° (decomp.), has been isolated, which is hydrolysed to a mixture consisting mainly of (**II**) with some (**IV**). Both the latter bases occur in dimorphic forms, the respective pairs being indistinguishable.

IV. The glycosidic moiety of (**III**) consists of glucose, rhamnose, and galactose. F. R. S.

Sinomenine. XLVII. (+)-Dihydrocodeine and (+)-dihydromorphine from sinomenine. K. Goto and T. Arai (*Annalen*, 1941, **547**, 194—200).—(+)-Dihydrocodeinone (demethoxydihydrosinomeneine) is hydrogenated at room temp. in C_5H_5N containing PtO_2 to (+)-*dihydrocodeine* (**I**) (+$2H_2O$), m.p. 87—88°, (anhyd.) m.p. 110°, $[\alpha]_D^{30}$ +146·4° in EtOH (*methiodide*, m.p. 257°, $[\alpha]_D^{30}$ +80·1° in H_2O). Admixture of (**I**) with an equal quantity of its (−)-isomeride gives dl-*dihydrocodeine*, m.p. 105°, $[\alpha]_D$ ±0° (*methiodide*, m.p. 257°). (**I**) is demethylated by boiling HI (*d* 1·7) to (+)-*dihydromorphine*, m.p. 159°, $[\alpha]_D^{30}$ +151·5° in EtOH (*hydriodide*, m.p. 285°, $[\alpha]_D^{29}$ +87·9° in H_2O; *methiodide*, m.p. 245°, $[\alpha]_D^{31}$ +74·9° in H_2O). Similarly, (−)-dihydrocodeine gives (−)-*dihydromorphine*, m.p. 159°, $[\alpha]_D^{30}$ −149·7° in EtOH (*hydriodide*, m.p. 285°, $[\alpha]_D^{28}$ −85·8° in H_2O; *methiodide*, m.p. 245°, $[\alpha]_D^{30}$ −75·1° in H_2O). dl-*Dihydromorphine* has m.p. 154° (*hydriodide*, m.p. 261°; *methiodide*, m.p. 267°). (**I**) and PCl_5 afford (+)-*dihydrochlorocodide* (**II**), m.p. 173°, $[\alpha]_D^{28}$ +177·2° in $CHCl_3$ (*methiodide*, m.p. 248°, $[\alpha]_D^{7}$ +114·8° in EtOH). dl-*Dihydrochlorocodide* has m.p. 146°, $[\alpha]_D$ ±0° (*methiodide*, m.p. 253°). Na in MeOH at 140° converts (**II**) into (+)-*deoxycodeine* C, m.p. 103°, $[\alpha]_D^{20}$ +179·6° in MeOH (*methiodide*, m.p. 238°, $[\alpha]_D^{13}$ +102·4° in 90% MeOH). (−)-Deoxycodeine *C* has m.p. 103°, $[\alpha]_D^{20}$ −177·8° in EtOH (methiodide, m.p. 240°, $[\alpha]_D^{13}$ −102·6° in 90% MeOH). dl-*Deoxycodeine* C, m.p. 85°, $[\alpha]_D$ ±0°, and its *methiodide*, m.p. 218°, are described. H. W.

VIII.—ORGANO-METALLIC COMPOUNDS.

Sulphophenylarsinic acids and their derivatives. V. 4′-Sulpho- and 4′-sulphamyl-diphenyl-4-arsinic acids. J. F. Oneto and E. L. Way (*J. Amer. Chem. Soc.*, 1941, **63**, 3068—3070; cf. A., 1941, II, 178).—*p*-$C_6H_4Ph{\cdot}AsO_3H_2$ (prep. from the amine by the Scheller reaction or as by-product in the prep. of $AsPhO_3H_2$ by the " Bart " reaction), m.p. >360° (derived di-iodoarsine, m.p. 109—110°), with 96% H_2SO_4 at 110—120° gives 4′-*sulphodiphenyl-4-arsinic acid* (**I**), anhyd. and +H_2O (*Ba* salt), or with $ClSO_3H$ at <20° and later 100° gives 4′-$SO_2Cl{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}AsO_3H_2$-4 (**II**). In boiling H_2O, (**II**) gives (**I**), and with boiling 10% aq. NH_3 gives *NH₄ H* 4′-*sulphamyldiphenyl-4-arsinate* and thence 4′-*sulphamyldiphenyl-4-arsinic acid* (**III**). The *Na* salt of (**I**) with 50% aq. HI and AcOH at room temp. gives *Na* 4-*di-iodoarsinodiphenyl-4′-sulphonate*, decomp. when heated, and thence by 10% aq. NH_3 the derived *arsine oxide Na* salt. In 50% HI and AcOH at 75—80°, (**III**) gives 4′-*sulphamyldiphenyl-4-di-iodoarsine*, m.p. >200°, and thence the *arsine oxide*. Structures are proved by conversion of (**I**) by 50% HI at 100° into *p*-$C_6H_4Ph{\cdot}SO_3H$, identified by conversion of its Cu salt by PCl_5 into the acid chloride. R. S. C.

IX.—PROTEINS.

New method of fractionation of proteins by electrophoresis convection. J. G. Kirkwood (*J. Chem. Physics*, 1941, **9**, 878—879).—Fractionation of proteins electrophoretically is suggested and the theory of the method is outlined. Preliminary investigations with mixtures of ovalbumin and hæmoglobin indicated significant separation. W. R. A.

Partial acid hydrolysis of proteins, with reference to mode of linkage of basic amino-acids. A. H. Gordon, A. J. P. Martin, and R. L. M. Synge (*Biochem. J.*, 1941, **35**, 1369—1387).—Wool, edestin, and gelatin are partly hydrolysed by digestion with 10N-HCl at 37° for 139—192 hr., and the products are submitted to electrodialysis. A large proportion of the basic NH_2-acids have thus been isolated as dipeptides, in the case of arginine 80—92%. About ⅓ of the residues are liberated as free NH_2-acids, so that basic NH_2-acids are more resistant. Cystine in edestin is set completely free. The bearing of the results on protein structure is discussed. P. G. M.

Chemistry of insect cuticle. I. Anthropod cuticles and characterisation of their proteins.—See A., 1942, III, 247.

Supposed occurrence of hydroxyglutamic acid in milk-proteins.—See A., 1942, III, 315.

Methylaspartic acids and their methylation.—See A., 1942, II, 132.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Lignin and related compounds.—LV, LVI, LX.—See A., 1942, II, 143.

Lignin and related compounds. LVII. Mechanism of the ethanolysis reaction. LVIII. Mechanism of the ethanolysis of maple wood at high temperatures. W. B. Hewson, J. L. McCarthy, and H. Hibbert. **LXI. Hydrogenation of ethanolysis fractions from maple wood. II.** L. M. Cooke, J. L. McCarthy, and H. Hibbert. **LXII. High pressure hydrogenation of wood using copper chromite catalyst. I.** H. P. Godard, J. L. McCarthy, and H. Hibbert. **LXIII. Hydrogenation of wood. II.** J. R. Bower, jun., J. L. McCarthy, and H. Hibbert (*J. Amer. Chem. Soc.*, 1941, **63**, 3041—3045, 3045—3048,

3056—3061, 3061—3066, 3066—3068; cf. A., 1942, II, 42).—LVII. Grinding maple wood before or during ethanolysis does not increase above the usual 30% the amount of H_2O-sol., distillable oil (*A*) obtained. Repeated treatment of the wood for short periods with small amounts of HCl–EtOH removes nearly all the lignin. The EtOH-sol. lignin produced by ethanolysis is partly converted by HCl–EtOH into a less sol. lignin. Ethanolysis of lignin thus consists of depolymerisation and subsequent partial polymerisation.

LVIII. Dry EtOH at 150°, 165°, 180°, or 200° extracts the lignin from maple wood only slowly. Addition of small amounts of NaOH or HCl very greatly accelerates the extraction at these temp. as well as at 78°. 1 : 1 aq. EtOH extracts much more than dry EtOH. H_2O at 165° is ineffective, but 2% aq. NaOH is very effective. The yields of (*A*) are less at high than at low temp. Thus, the EtOH-sol. unimol. compounds do not exist in lignin as such but rather combined with each other (*e.g.*, as ethers) and possibly also with carbohydrates. Fission of these aggregates is due to H^+ or OH', the effect of H_2O being to increase the ionisation of EtOH etc., increase of temp. and presence of an appropriate solvent facilitating the process. Formation of EtOH-sol. and -insol. lignins is subsequent to this fission.

LXI. H_2–Cu chromite converts the main maple EtOH-lignin fraction in dioxan at 250°/3400 lb. into H_2O 13·6, MeOH 5·0, EtOH 8·7, 4-*n*-propyl*cyclo*-hexanol (**I**) 8·1, and -hexane-1 : 2-diol 1·9, γ-4-hydroxy*cyclo*hexylpropan-α-ol (**II**) 3·3, a H_2O-insol. *compound* (**III**), b.p. 130—132°/1 mm., 2·1, and high-boiling resins 29·5%. Difference in the yield of (**II**) from that obtained from aspen MeOH-lignin (Harris *et al.*, A., 1938, II, 332) indicates a possible difference in structure. Similar experiments with other fractions indicate that ease of fission to propylphenol units increases with increasing solubility of the fraction. Probably these units are linked by C·O·C in the easily split and by C·C linkings (polymerisation) in the difficultly split portions. The C·O·C linkings may be of acetal type.

LXII. H_2–Cu chromite converts spruce or maple wood in dioxan at 280°/3500 lb. entirely into colourless liquid products, including (**I**) 19·5 and (**II**) 5·8% (calc. on Klason lignin). The recovery of propylphenol units is calc. to be 36%.

LXIII. Maple wood holocellulose is hydrogenated (Cu chromite) at 280°/3500 lb. Comparison of the results with those of the preceding paper indicates that (**I**), (**II**), and (**III**) are derived from the lignin and that a fraction, b.p. 70—125°/20 mm., is derived from the protolignin. R. S. C.

XI.—ANALYSIS.

New form of chromatogram employing two liquid phases. I. Theory of chromatography. II. Application to micro-determination of higher monoamino-acids in proteins.—See A., 1942, I, 160.

Sample carrier for organic liquids.—See A., 1942, I, 159.

Disposal of acid fumes [in micro-Kjeldahl digestions].—See A., 1942, I, 159.

Micro-gasometric determination of nitrogen.—See A., 1942, III, 360.

Determination of total sulphur in organic liquids, using a semi-micro-method. E. B. Lisle (*J.S.C.I.*, 1942, **61**, 20).—The S compound is oxidised to SO_2 by passing the vapour of the compound mixed with O_2 or air over red-hot Pt gauze. The SO_2 is passed over filter-paper impregnated with $Ni(OH)_2$, which is converted into black Ni, the depth of colour being ∝ amount of SO_2 present.

Improved semimicro-determination of sulphur in organic materials. Peroxide-carbon fusion followed by a titration using tetrahydroxy-[benzo]quinone indicator. J. F. Mahoney and J. H. Michell (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 97—98).—The S compound is fused with Na_2O_2–sugar C, and the fused mass dissolved in 12N-HCl, neutralised with aq. 16N-NH_3, an indicator of tetrahydroxybenzoquinone–$AgNO_3$ added, and the mixture titrated with $BaCl_2$. 0·5—5 mg. of S can be determined rapidly and accurately. J. D. R.

Determination of mercury in organic compounds. Iodometric procedure based on the method of Rupp. H. A. Sloviter, W. M. McNabb, and E. C. Wagner (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 890—893).—The sample is digested with $K_2S_2O_8$–H_2SO_4 and the $HgSO_4$ produced is treated with KBr–$KBrO_3$, followed by aq. KI and aq. NaOH. The Hg is now pptd. with aq. N_2H_4 in presence of Na_2CO_3–$MgSO_4$, and the Hg collected and dissolved in known excess of KBr–$KBrO_3$, KI added, and the excess of I titrated with $Na_2S_2O_3$. The high results obtained by Rupp's method, in which CH_2O is the reducing agent, are probably due to reduction of some I by HCO_2H produced from CH_2O during pptn. of Hg or by Cannizzaro reaction. J. D. R.

Colour reaction for sulphurous acid, the thiol group, and formaldehyde. A. Steigmann (*J.S.C.I.*, 1942, **61**, 18—19).—The dye resulting from the action of CH_2O on fuchsin–H_2SO_3 is much more resistant towards strong mineral acids than are plain fuchsin solutions, which are almost decolorised by conc. H_2SO_4. Addition of aq. CH_2O to such a discoloured solution produces but little change; further addition of traces of aq. SO_2 develops an intense pink-violet colour. A diluted fuchsin solution containing much H_2SO_4 and some CH_2O is therefore a delicate and simple reagent for H_2SO_3. Thio-acids can be used in place of H_2SO_3; the new reagent is therefore useful also for the detection of thio-acids. Decolorised fuchsin–H_2SO_4 solution, with $SH{\cdot}CH_2{\cdot}CO_2H$ instead of H_2SO_3, is furthermore a selective CH_2O reagent. The new reagents may be used in conjunction with Feigl's I–azide reagent for SH in mercaptans and thio-acids.

Identification of organic acids by use of *p*-bromobenzyl-ψ-thiuronium bromide.—See A., 1942, II, 129.

Determination of citric acid in pure solutions and in milk by the pentabromoacetone method. E. F. Deysner and G. E. Hoem (*Ind. Eng. Chem.* [*Anal.*], 1942, **12**, 4—7; cf. Lampitt and Rooke, B., 1936, 1229).—Citric acid (**I**) is determined by oxidation with $KMnO_4$ in presence of KBr, which converts (**I**) into $CBr_3{\cdot}CO{\cdot}CHBr_2$ (**II**), the former method being modified by using an excess of $KMnO_4$ to ensure complete oxidation. Data are presented on the solubility of (**II**) in H_2O, with consequent loss by washing, and on loss in wt. of (**II**) by drying. No abs. method of determining (**I**) can be prescribed, and the method must be standardised for each material analysed. J. D. R.

Determination of citric acid.—See A., 1942, III, 360.

New and highly specified colorimetric test for methionine. T. E. McCarthy and M. X. Sullivan (*J. Biol. Chem.*, 1941, **141**, 871—876).—To 5 c.c. of the solution under examination are added successively 1 c.c. of 14·5N-NaOH, 1 c.c. of 1% glycine (**I**), and 0·3 c.c. of 10% aq. Na nitroprusside with mixing after each addition. The mixture is heated at 35—40° for 5—10 min., cooled in ice-water for 2 min., and treated with shaking with 5 c.c. of HCl–H_3PO_4 mixture (9 vols. of conc. HCl + 1 vol. of 85% H_3PO_4). Shaking is continued for 1 mm., after which the solution is cooled in H_2O at room temp. for 5—10 min. and the colour is matched against a standard solution of methionine (**II**) similarly treated. The use of conc. NaOH + (**I**) inhibits the colour due to histidine and HCl + H_3PO_4 gives a clearer colour than HCl alone. The reaction is highly sp. for (**II**) and is negative for all other NH_2-acids found in the acid hydrolysates of protein. Methionine sulphoxide is negative, as are homocystine, cystine, and cysteine, but glycylmethionine is positive. If the solution is kept cold at the time of addition of the acid no colour reaction is given by tryptophan even if present in considerable amount. The application of the test to the determination of the content of (**II**) in casein and edestin is described. H. W.

Determination of choline. Photometric modification of Beattie's method. M. H. Thornton and F. K. Broome (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 39—41).—The solution of choline (**I**) is pptd. with $NH_4[Cr(NH_3)_2(CNS)_4]$ and the ppt. dissolved in $COMe_2$. The concn. of the salt of (**I**) in the solution is determined photocolorimetrically. Concns. of (**I**) of 0·3—6·5 mg. per c.c. can be determined with a max. error of 2%. J. D. R.

Micro-determination of arginine. J. B. Dubnoff (*J. Biol. Chem.*, 1941, **141**, 711—716).—For complete separation of glycocyamine (**I**) and arginine (**II**) the salt concn. of the solution should be ≯ 0·5%. If neither compound is present in amount >2 mg.-%, the salt concn. may be as high as 1%. Urine is usually diluted 5—10 times with H_2O. Blood filtrates may be prepared by deproteinising according to Folin and Wu or by heat-coagulation at p_H 6 after 1 : 10 dilution with H_2O. Tissue extracts are diluted to contain 1 g. of fresh tissue in 40 ml. of suspension. The p_H is adjusted to 6·0 and the suspension immersed in boiling H_2O for 10 min., cooled, and filtered. Analyses are carried out on the filtrates. 5 ml. of the solution to be analysed are passed through the permutit column and the small amount of (**I**) remaining in the column is removed with 5 ml. of 0·3% NaCl. The combined filtrates contain all the (**I**). (**II**) is eluted by passing 10 ml. of 3% NaCl through the column. A 2-ml. portion is cooled in ice and treated with 0·5 ml. of the ice-cold $C_{10}H_7{\cdot}OH$–$CO(NH_2)_2$ solution; after 2 min. 0·2 ml. of ice-cold NaOBr solution is added. The colour is simultaneously developed in a series of standards containing 0, 0·25, 0·5, 1·0, and 2·0 mg.-% of (**II**). After 20 min. the development of colour is complete and remains stable for 2 hr. at 0°. The tubes are shaken for a few sec. to remove excess of gas, warmed to room temp., and the intensity of the colour is measured in a spectrophotometer or colorimeter with light of ~0·525 μ. (yellow-green). H. W.

Determination of adenine. G. H. Hitchings and C. H. Fiske (*J. Biol. Chem.*, 1941, **141**, 827—835).—Adenine and, under certain conditions, guanine can be determined by pptn. with Na picrate and titration of the ppts. with standard NaOH. H. W.

Chlorosulphonic and as reagent for identification of alkylbenzenes.—See A., 1942, II, 136.

Photo-electric determination of nicotinic acid.—See A., 1942, III, 254.

Determination of adenosine-5′-phosphoric acid and its homologues.—See A., 1942, III, 183.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

MAY, 1942.

I.—ALIPHATIC.

Alkylation of paraffins at low temperatures in the presence of aluminium chloride. H. Pines, A. V. Grosse, and V. N. Ipatieff (*J. Amer. Chem. Soc.*, 1942, **64**, 33—36; cf. U.S.P. 2,112,846, B., 1941, II, 31).—$CHMe_3$ and CH_2:CHEt in presence of $AlCl_3$ at −35° (apparatus described) yield 60% of C_8H_{18} and 12% of $C_{12}H_{26}$. The former are identified by Raman spectra as $CHMeEtBu^{\gamma}$ (a primary reaction product), $CH_2Pr^{\beta}Bu^{\gamma}$ and $(CH_2Pr^{\beta})_2$ (formed by preliminary isomerisation of *n*- to *iso*-C_4H_8), and $CHMePr^{\beta}_2$ (formed by isomerisation of other octanes). $CHMe_3$ and C_3H_6 give similarly 42% of C_7H_{16} and 20% of $C_{10}H_{22}$. The C_7H_{16} are similarly shown to contain $CHMeEtPr^{\beta}$ and some $CH_2Pr^{\beta}_2$. R. S. C.

Production of *iso*paraffins.—See B., 1942, II, 46.

Photolysis of methyl bromide.—See A., 1942, I, 179.

Chlorination of chloroform to carbon tetrachloride in presence of ferric chloride.—See A., 1942, I, 177.

Separation of olefines from mixtures of hydrocarbons.—See B., 1942, II, 47.

Low-temperature polymerisation of *iso*olefines.—See B., 1942, II, 47.

Production of hydrocarbons of high mol. wt. [from *iso*butene].—See B., 1942, II, 47.

Structure and absorption spectra. III. Normal conjugated dienes. R. B. Woodward (*J. Amer. Chem. Soc.*, 1942, **64**, 72—75; cf. A., 1941, II, 195).—Absorption max. of normal conjugated dienes (*i.e.*, those in which the ethylenic linkings are not in one ring) are accurately calc. by adding to $\lambda_{max.}$ (217 mμ.) for $(CH{:}CH_2)_2$ 5 mμ. for each substituent and 5 mμ. for each exocyclic ethylenic linking. The substance previously (Booker *et al.*, A., 1940, I, 27) considered to be $\Delta^{3:8(9)}$-normenthadiene probably consists mainly of the $\Delta^{\cdot 2:4(8)}$-compound. R. S. C.

Course of autoxidation reactions in polyisoprenes and allied compounds. II. Hydroperoxidic structure and chain scission in low-molecular polyisoprenes. E. H. Farmer and D. A. Sutton (*J.C.S.*, 1942, 139—148).—Progressive determinations of O_2 intake and peroxidic O content and measurements of I val. show that in the autoxidation of squalene (**I**) (in C_6H_6), dihydrofarnesene (**II**), and dihydromyrcene (**III**), the primary reaction is the production of a hydroperoxide group, which in (**I**) and (**II**) reacts with double linkings giving OH-compounds and (to a small extent) scission products. Low O_2 intake is compatible with advanced oxidation of parts of the mol. Some subsidiary chain scission appears to occur at single linkings. (**II**) does not undergo any saturation during autoxidation. Reduction (Al–Hg + H_2O–Et_2O–EtOH) of the products from (**III**) yields a mixture containing *hydroxy-*, b.p. 90—103°/12 mm., and (mainly 1 : 2)*dihydroxy-dihydromyrcene*, b.p. (?) 115°/1 mm. (Cf. A., 1942, II, 170.) A. Li.

Rubber, polyisoprenes, and allied compounds. I. Synthesis of low-molecular polyisoprenes of the rubber and squalene type. E. H. Farmer and D. A. Sutton (*J.C.S.*, 1942, 116—121).—Geranylacetone with MgEtBr in Et_2O yields *dihydronerolidol* (**I**), b.p. 137—140°/8 mm., dehydrated ($KHSO_4$) to *dihydrofarnesene*, b.p. 129—131°/11 mm. [*trihydrochloride* (**II**), m.p. 52°, also obtained from (**I**) and anhyd. HCl], which with Br in $CHCl_3$ yields an oil, and with O_3 gives $COMe_2$ and its peroxide, MeCHO, and AcOH, but no CH_2O, HCO_2H, or COMeEt. Dehydration ($KHSO_4$) of farnesol, reduction (Na + EtOH) of the product, and treatment with HCl yields a mixture of bisabolene trihydrochloride and (**II**). (**I**) with $MgBr{\cdot}[CH_2]_4{\cdot}MgBr$ in Et_2O yields *dihydroxydihydrosqualene*, b.p. 220—235°/1 mm., which with HCl in Et_2O gives a mixture of the three hydrochlorides obtained similarly from squalene. A. Li.

Separation of divinylacetylene and ethinylbutadiene and purification of the latter.—See B., 1942, II, 47.

Identification of alcohols in aqueous solution. W. N. Lipscomb and R. H. Baker (*J. Amer. Chem. Soc.*, 1942, **64**, 179—180).—Aliphatic alcohols are isolated from aq. solution as 3 : 5-dinitrobenzoates by shaking with the acid chloride, aq. NaOAc, NaOH, and C_6H_6–light petroleum at 0°. R. S. C.

Vapour-phase partial oxidation of ethyl alcohol.—See A., 1942, I, 177.

iso- and *n*-**Butyl alcohols from carbide.**—See B., 1942, II, 45.

Oxychlorides of silicon and corresponding ethyl esters.—See A., 1942, I, 152.

Purification of glycols.—See B., 1942, II, 48.

Chain structure of linear polyesters. Trimethylene glycol series.—See A., 1942, I, 136.

(A) **Structure of (αγδζ-)dibenzylidenedulcitol.** (B) **(βγδε-)Dibenzylidenedulcitol.** (C) **Second βγδε-dibenzylidenedulcitol.** W. T. Haskins, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 132—136, 136—137, 137—140).—(A) Fischer's dibenzylidenedulcitol (**I**) (modified prep.; A., 1894, 395) is proved to be the αγδζ-compound. $Pb(OAc)_4$–AcOH attacks (**I**) very slowly. With Ac_2O–C_5H_5N or RCOCl–C_5H_5N, (**I**) gives the *βε-diacetate*, decomp. 265°, *-dichloroacetate*, decomp. 228—229°, *-dibenzoate* (**II**), decomp. 285°, and *-di-p-toluenesulphonate* (**III**), m.p. 215° (decomp.). With Ac_2O–AcOH–(drop) H_2SO_4, (**II**) gives *dulcitol βε-dibenzoate αγδζ-tetra-acetate*, m.p. 157—158°. In boiling C_5H_5N, (**III**) is unchanged and βγδε-di*iso*propylidenedulcitol αζ-di-*p*-toluenesulphonate (**IV**) gives a $(C_5H_5N)_2$ compound, m.p. 199—200°. NaI–Ac_2O has no effect on (**III**) but converts (**IV**) into the αζ-di-iodide. In boiling aq. N-HCl-dioxan, (**II**) gives dulcitol αζ-dibenzoate (**V**) (15), *dl*-galactitol αδ-dibenzoate (29%), and a syrup (56%). With Na and then CH_2PhCl in boiling dioxan, (**I**) gives the *βε-$(CH_2Ph)_2$ ether* (**VI**), decomp. 246—250°, hydrolysed by boiling aq. N-HCl–dioxan to *dulcitol βε-$(CH_2Ph)_2$ ether*, m.p. 168—169°, which consumes 1 HIO_4, giving no CH_2O, and consumes 1 $Pb(OAc)_4$, giving *dl*-glyceraldehyde *β*-CH_2Ph ether (*semicarbazone*, m.p. 132—134°). (**VI**) is accompanied by some *β-CH_2Ph ether*, m.p. 164—165° (*ζ-acetate*, m.p. 204—206°).

(B) Passage of HCl into (**V**) and PhCHO gives *βγδε-dibenzylidenedulcitol αζ-dibenzoate* (**VII**), m.p. 119—120°, converted by Ac_2O–AcOH–H_2SO_4 into dulcitol βγδε-tetra-acetate αζ-dibenzoate (**VIII**) and by NaOMe–MeOH–$CHCl_3$ at 5° into 2 : 3 : 4 : 5-*dibenzylidenedulcitol* (**IX**), m.p. 149—150°, the *αζ-diacetate* (**X**), m.p. 168—169°, of which (prep. by Ac_2O–C_5H_5N) is also obtained from dulcitol αζ-diacetate by HCl–PhCHO.

(C) PhCHO, (**V**), and $ZnCl_2$ (pure) at 23—25° (not 60°) give only 17% of (**VII**) and 67% of a (? *stereo*)*isomeride* (**XI**), m.p. 147—148°. PhCHO–$ZnCl_2$ converts (**XI**) into (**VII**), and Ac_2O–AcOH–H_2SO_4 gives (**VIII**). With NaOMe–MeOH–$CHCl_3$ at 5°, (**XI**) gives a *βγδε-dibenzylidenedulcitol* (**XII**), m.p. 173—174° [*αζ-diacetate*, m.p. 167—168°, converted into (**X**) by PhCHO–$ZnCl_2$ at 60°]. (**VII**) and (**XII**) give *αζ-$(CPh_3)_2$ ethers*, m.p. 184—186° and 240—242°, and *αζ-di-p-toluenesulphonates*, m.p. 167—168° and 175—176°, and thence (NaI–Ac_2O) *αζ-di-iodides*, m.p. 127—128° and 162—163°, respectively. M.p. (all papers) are corr. R. S. C.

Use of Bunte salts in synthesis. III. Preparation of aliphatic disulphides. H. E. Westlake, jun., and G. Dougherty (*J. Amer. Chem. Soc.*, 1942, **64**, 149—150; cf. A., 1941, II, 184).—$NaRS_2O_3$ (prep. *in situ*) with I or H_2O_2 in aq. EtOH give R_2S_2, yields being R = Bu^{α} 57, 56, n-*heptyl* (b.p. 143—147°/5 mm.) 66, 65, n-*octyl* (b.p. 178—183°/5 mm.) 69, 52, n-*dodecyl* 35, ~70, and *n*-octadecyl 49%, —, respectively. R. S. C.

Aliphatic sulphinic acids. I. Analysis and identification. P. Allen, jun. (*J. Org. Chem.*, 1942, **7**, 23—30).—*Mg alkanesulphinates*, $(RSO_2)_2Mg.2H_2O$ (R = Me to $C_{16}H_{33}$ inclusive), are obtained from the requisite Grignard reagent and SO_2. They are insol. in EtOH; the lower members are sparingly sol. in hot H_2O but the higher ones are insol. They are very readily electrified by friction. They are stable in H_2O at room temp. for several days but are quickly oxidised when heated. The Na salts are obtained from the Mg compounds and Na_2CO_3 or NaOH or by neutralising the free sulphinic acid with Na_2CO_3. Owing to their ready oxidisability, they could not be obtained quite pure. Dry Na and Mg salts are stable in air. Titration of the salts with oxidising agents in acid medium leads to only ~80—90% of the theoretical vals. In alkaline solution they can be accurately titrated potentiometrically with $KMnO_4$ or $Ca(OCl)_2$. Another convenient method is to add an excess of $KMnO_4$ to the alkaline solution followed by sufficient As_2O_3 to react with the MnO_2 and extra $KMnO_4$; the solution is acidified and, after disappearance of the MnO_2, is titrated with $KMnO_4$ to the colorimetric or potentiometric end-point. In neutral solution

potentiometric titration gives results almost but not quite so good as those obtained in alkaline solution. The higher Mg salts require a preliminary digestion (40—60 min.) with dil. NaOH without or with an insufficiency of $KMnO_4$, after which the mixture is titrated hot to the potentiometric end-point. The Na salts are transformed by $(CH_2Br)_2$ in boiling EtOH into *αβ-dialkylsulphonylethanes*, $(n\text{-}R{\cdot}SO_2{\cdot}CH_2{\cdot})_2$, in which R = Me, m.p. 190°, Et, m.p. 136—137°, Pr^n, m.p. 159·3—160·3°, Bu^n, m.p. 179·2—180·2, *amyl*, m.p. 183·7—184·2°, *hexyl*, m.p. 177·5—178·5°, *heptyl*, m.p. 176—177·5°, *octyl*, m.p. 172·8—173·5°, *nonyl*, m.p. 172·5—173·5°, *decyl*, m.p. 169·9—170·9°, *undecyl*, m.p. 168·3—169·3°, *dodecyl*, m.p. 165·8—166·8°, *tridecyl*, m.p. 163·4—164·1°, *tetradecyl*, m.p. 160·9—161·9°, *pentadecyl*, m.p. 158·7—159·9°, *hexadecyl*, m.p. 154·6—155·8°. The requisite Na sulphinate and EtI in boiling EtOH afford *Et undecyl*, m.p. 76·5—77·5°, *dodecyl*, m.p. 75·0—76·0°, and *hexadecyl*, m.p. 77·0—79·0°, *sulphone*. H. W.

Manufacture of aliphatic acids and their anhydrides.—See B., 1942, II, 48.

Production of esters.—See B., 1942, II, 49.

Manufacture of β-chloropropionic acid.—See B., 1942, II, 49.

Hexoic acid esters.—See B., 1942, II, 49.

Synthesis of methylated fatty acids. A. K. Schneider and M. A. Spielman (*J. Biol. Chem.*, 1941, **142**, 345—354).—*cyclo*Hexanone and n-$C_{12}H_{25}$·MgBr afford 1-*dodecyl*-Δ^1-cyclo*hexene* (43% yield), b.p. 140—143°/1·5 mm., oxidised by CrO_3–aq. AcOH to ε-ketostearic acid (43% yield), m.p. 86·5—87°, reduced (Clemmensen) to stearic acid. n-$C_{12}H_{25}$·MgBr–$ZnCl_2$–Et_2O and COCl·$[CH_2]_8$·CO_2Et in C_6H_6 (in N_2) yield *ι-ketodocosanoic acid*, m.p. 91·5° (62% yield), converted by Zn–Hg in EtOH nearly saturated with HCl into n-docosanoic acid, m.p. 79—80·5° (85% yield). Similarly prepared are *ι-ketotetracosanoic acid*, m.p. 94—94·5°, and n-tetracosanoic acid, m.p. 82·5—83·5°. $CHMe(CO_2Et)_2$–NaOBu^n–n-$C_{16}H_{33}$I afford the Et_2 ester and thence the dicarboxylic acid, decarboxylated at 150—180°/10 mm. to α-methylstearic acid, new m.p. 54·5° (amide, m.p. 104·5°). Similarly prepared are *α-methyl-eicosanoic acid*, m.p. 61·5—62° (*amide*, m.p. 108°), *-docosanoic acid*, m.p. 67—67·5° (*amide*, m.p. 109—109·5°), *-tetracosanoic acid*, m.p. 72—72·5° (*amide*, m.p. 111·5°), and *-hexacosanoic acid*, m.p. 75·5—76° (*amide*, m.p. 113°). Et ι-ketoundecoate, b.p. 153—154°/6 mm., and n-$C_{14}H_{29}$·MgBr–Et_2O (in N_2) at 25° afford, through the resulting ester, a carboxylic acid, dehydrated at 180—210° (+ a trace of I) and then hydrogenated (Pt, or Raney Ni at 175°/160 atm., in EtOH) and hydrolysed, to give *ι-methyltetracosanoic acid*, m.p. 51° (*amide*, m.p. 79—79·5°); *ι-methyl-docosanoic acid*, m.p. 45·5—46° (*amide*, m.p. 78—78·5°), and *-hexacosanoic acid*, m.p. 54—55° (*amide*, 81—81·5°), are also prepared. Morpholine acetate and CHMe:CH·CHO give a mixture of polymerides, which after hydrogenation (Raney Ni) yield only n-C_8H_{17}·OH and n-$C_{12}H_{25}$·OH. A. T. P.

Long-chain acids. III. Bisnoroleic acid. P. C. Mitter and P. N. Bagchi (*J. Indian Chem. Soc.*, 1941, **18**, 461—464; cf. A., 1940, II, 203).—Me oleate and MgMeI give *αα-dimethyl-Δ^ι-octadecen-α-ol*, b.p. 167—172°/3 mm., converted by successive treatments with Br–AcOH, CrO_3–AcOH, Zn–AcOH, and MeOH–H_2SO_4 into *Me* Δ^η-*heptadecenoate* (*Me noroleate*), b.p. 159—165°/6 mm., which with MgMeI yields *αα-dimethyl-Δ^0-heptadecen-α-ol*, b.p. 160—164°/4 mm., and thence, by successive stages as above, *Me* Δ^ι-*hexadecenoate* (*Me bisnoroleate*), b.p. 150—155°/6 mm. (low yield). A. T. P.

Preparation of α-hydroxycarboxylic acids.—See B., 1942, II, 49.

Influence of halides on oxidation of ascorbic acid.—See A., 1942, III, 329.

Photochemical oxidation of chloral sensitised by bromine.—See A., 1942, I, 179.

Production of unsaturated aliphatic aldehydes.—See B., 1942, II, 50.

Syntheses in the carotenoid series. V. Preparation of higher aliphatic polyenealdehydes. J. Schmitt and A. Obermeit (*Annalen*, 1941, **547**, 285—292).—Self-condensation of crotonaldehyde (I) by piperidine acetate in 70% EtOH [whereby OEt is not introduced (cf. lit.)] at room temp. gives dodecapentaenal (II), m.p. 165°. Sorbaldehyde and (I) give *tetradecahexaenal*, m.p. 192°, converted into palmitic acid by way of Me·[CH:CH]$_6$·CH:C(CO_2H)$_2$ and Me·[CH:CH]$_7$·CO_2H. In 70% EtOH, (I) and (II) give hexadecaheptaenal, m.p. 216—217°, but in C_5H_6 some eicosanonaenal is also formed. R. S. C.

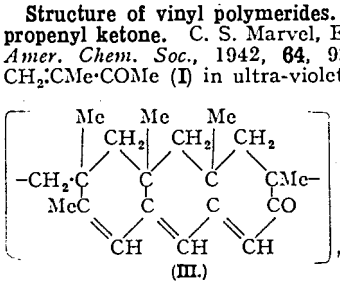
Preparation of glyceraldehyde α-methyl ether.—See B., 1942, II, 50.

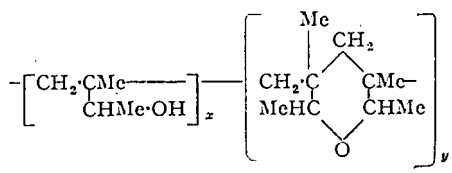
Photolysis of keten in presence of hydrogen and methane.—See A., 1942, I, 179.

Manufacture of unsaturated ketones and ketonic resins.—See B., 1942, II, 51.

Thermal decomposition of acetone catalysed by iodine.—See A., 1942, I, 176.

Structure of vinyl polymerides. XII. Polymeride of methyl *iso*propenyl ketone. C. S. Marvel, E. H. Riddle, and J. O. Corner (*J. Amer. Chem. Soc.*, 1942, **64**, 92—94; cf. A., 1941, II, 83).—CH_2:CMe·COMe (I) in ultra-violet light or with Bz_2O_2 at 25° gives polymerides, mol. wt. (II) 11,200 and ~36,000, respectively; at 60° in $COMe_2$ it gives a polymeride, mol. wt. ~6000, or without a solvent ~12,000 (cf. Staudinger *et al.*, A., 1936, 1336). The products are obtained solid by adding the $COMe_2$ solution to H_2O (<100 c.c. per g. of polymeride). The head-to-tail structure, $[\cdot CH_2{\cdot}CMeAc\cdot]_n$, of (II) is proved by pyrolysis at 270—300° or 360° to H_2O and a $COMe_2$-sol. *polymeride* (III) {and a little (I) and COMe·CHMe·$[CH_2]_2$·CO·CMe:CH_2} with loss of 63% of


(III.)


(IV.)

the O, random ring-closure requiring loss of 68·8%. This structure is confirmed by hydrogenation (Raney Ni; dioxan; 175°/2000 lb.) to the *compound* (IV) (86·47% ring-closure), m.p. 195—205°; the structure of (IV) is in turn proved by analysis of the *acetate* and *chloroacetate*, (prep. in C_5H_5N). R. S. C.

Structure and absorption spectra. IV. αβ-Unsaturated ketones. R. B. Woodward (*J. Amer. Chem. Soc.*, 1942, **64**, 76—77; cf. A., 1942, II, 161).—In calculating absorption max. of αβ-, ββ-, or αββ-substituted αβ-unsaturated ketones, each substituent contributes 11 mμ. (not 15) and each exocyclic ethylenic linking an additional 5 mμ. The ketones, m.p. 94° and 37°, obtained from di-Δ^1-*cyclo*hexenylacetylene by HCO_2H are probably 3-pentamethylene-Δ$^{3(a)7(a)}$- and -Δ^7-hexahydroindone, respectively. R. S. C.

Cyclic methyleneimines. IV. Hydrolysis of quaternary compounds. Preparation of secondary amines. J. Graymore (*J.C.S.*, 1942, 29—30).—*NN'N''*-Trimethyltrimethylenetriamine (I) with $PhSO_2Cl$ in Et_2O yields *bis(benzenesulphonmethylamidomethyl)methylamine*, m.p. 122—123°, hydrolysed (dil. HCl or NaOH) to CH_2O, NH_2Me, $PhSO_2$·NHMe, and an unstable *product* (II), $C_9H_{22}N_4Cl_2$,4CH_2O, m.p. 118—120° (decomp.), hydrolysed to CH_2O and NH_2Me only. (I) with p-$C_6H_4Me{\cdot}SO_2Cl$ yields (II), p-$C_6H_4Me{\cdot}SO_2{\cdot}$NHMe, and *methylenebis-p-toluenesulphonmethylamide*, m.p. 117—118°, hydrolysed to CH_2O and p-$C_6H_4Me{\cdot}SO_2{\cdot}$NHMe. The mechanism of the reaction is discussed. A. Li.

4-Co-ordinated mercuric salts with diamines.—See A., 1942, I, 180.

Amino-derivatives of pentaerythritol. II. Thermal decomposition of the tetrahydrochlorides of tetrakismethylaminomethylmethane and tetrakisdimethylaminomethylmethane. G. M. Gibson, J. Harley-Mason, A. Litherland, and F. G. Mann. **III. Formation and thermal decomposition of some quaternary salts of tetrakisdimethylaminomethylmethane.** G. M. Gibson and F. G. Mann (*J.C.S.*, 1942, 163—175, 175—181; cf. A., 1938, II, 474).—II. The *tetrahydrochloride*, m.p. 264° (decomp.), of tetrakismethylaminomethylmethane {*dihydrate*, b.p. 245—248°; *tetrahydrobromide* [*monohydrate*, m.p. 266° (decomp.)]; ($PhSO_2$)$_4$ derivative, m.p. 239°} at 275° yields a mixture containing the *dihydrochloride*, m.p. 262—263°, of *αγ-bismethylaminopropane* (+H_2O), b.p. 141—144° (*dipicrate*, m.p. 193—194°) (synthesised from Br·$[CH_2]_3$·Br and aq. EtOH–NH_2Me at 120—130°). *Tetrakisaminomethyl-* (+4H_2O), m.p. 100—100·5°, with Me_2SO_4 yields *tetrakisdimethylaminomethyl-methane* (I), b.p. 248—249°/769 mm. [also prepared from $C(CH_2Br)_4$ and $NHMe_2$ in EtOH at 170°], the tetrahydrochloride (+3H_2O) of which when heated at 232—233° evolves H_2O and CH_2O, giving a mixture containing NH_2Me, $NHMe_2$, and NMe_3 hydrochlorides, and the *dihydrochloride* (II), m.p. 260° (decomp.) (unaffected by boiling dil. HCl), of a tert. *amine* (III), $C_8H_{18}N_2$, b.p. 150—154° [*dihydrobromide*, m.p. 243° (darkening); *dihydriodide*, m.p. 203—205° (previous softening); *dipicrate*, 185·5—187·5°; *bis*-d-α-*bromocamphor-π-sulphonate* (which could not be resolved), m.p. 170—176°, $[M]_D^{19}$ +556° in H_2O; *dimethiodide* (IV), m.p. 216—217° (decomp., preliminary darkening); *dimethochloride* (+H_2O) (V), m.p. 184—196° (efferv., resolidifying and remelting at 200°); *diaurichloride*, m.p. 237—238·5° (decomp.); *platinichloride*, m.p. 245° (decomp.); *dimethopicrate*, m.p. 257—257·5° (decomp.); *dimetho*-d-*camphorsulphonate* (which could not be resolved), m.p. 261—263° (slight softening), $[M]_D^{13}$ +101° in H_2O; *dibenzyliodide*, m.p. 168—169°; *dibenzylpicrate*, m.p. 199—201°]. (II) in *cyclo*hexane is slowly hydrogenated (PtO_2), rapidly after addition of AcOH. (III) in H_2O, or (IV) in MeOH, is completely hydrogenated to $CHMe_3$ and $NHMe_2$,HCl (or NMe_3,HCl) (no intermediate product isolable). Oxidation (alkaline $KMnO_4$) or (V) yields $H_2C_2O_4$ and CH_2O (no intermediate product isolable). O_3 does not affect (V), but decomposes (III), no CO-compound being

detected in the product. (**III**) with aq. Br gives only a perbromide (?), but (**II**) with Br in $CHCl_3$ yields the dihydrobromide of (**II**). $CHMe(CH_2Br)_2$ with EtOH–$NHMe_2$ at 130° yields *αγ-bisdimethylamino-β-methylpropane*, b.p. 151—152° (*dihydrochloride*, m.p. 233—234°; *dibenzylpicrate*, m.p. 169—171°), the *dimethiodide*, m.p. 267—268°, of which could not be reduced catalytically. $OH{\cdot}CH(CH_2Cl)_2$ with EtOH–$NHMe_2$ at 115—120° yields *αγ-bisdimethylaminoisopropyl alcohol*, b.p. 80—82°/17 mm. (*dimethiodide*, decomp. 250°), which could not be oxidised to the ketone. $CO(CH_2Cl)_2$ with MgMeBr yields *αγ-dichloro-β-methylisopropyl alcohol*, b.p. 71—72°/18 mm., which with β-$C_{10}H_7{\cdot}ONa$ gives *β-hydroxy-β-methyltrimethylene-αγ-bis-2-naphthyl ether*, m.p. 151—152°, and with EtOH–$NHMe_2$ at 115—125° yields *αγ-bisdimethylamino-β-methylisopropyl alcohol*, b.p. 80—81°/20 mm. [*dihydrochloride*, m.p. 250° (efferv.); *dipicrate*, m.p. 172—173°; *dimethiodide*, m.p. 176—177° (*monohydrate*, m.p. 105—110°)]. This could not be dehydrated, but with $SOCl_2$ in $CHCl_3$ yields *β-chloro-αγ-bisdimethylamino-β-methylpropane*, b.p. 81°/15 mm. (*dipicrate*, m.p. 155—156°). HCl could not be eliminated from this, which with EtOH–KOH yields *αγ-bisdimethylamino-β-ethoxy-β-methylpropane*, b.p. 91—92°/15 mm. [*dimethiodide*, m.p. 140—150° (efferv., previous softening)], but its *dimethiodide*, m.p. 195—196° (decomp.), with MeOH–KOH (1 mol.) affords *αγ-bistrimethylammonium-β-methylpropenylene di-iodide* (**VI**), m.p. 203—204° [corresponding *dimethopicrate*, (**VII**), m.p. 245—246° (decomp.)]. Excess of MeOH–KOH yields NMe_3,HI and a compound giving a 2 : 4-dinitrophenylhydrazone, m.p. 174—177°. (**VI**) is hydrogenated (PtO_2) quantitatively to NMe_3,HI and $CHMe_3$. Oxidation (alkaline $KMnO_4$) of (**VI**) yields $H_2C_2O_4$, also obtained (91%) from $AcCO_2H$. When boiled with H_2O–Ag_2O, (**IV**) or (**V**) yields a solution containing the ion $(^+NMe_2{\cdot}CH{:}CHMe{\cdot}CH_2)_2O$ (**VIII**) [*dipicrate*, m.p. 173—174°; *diaurichloride*, m.p. 201—202°; *platinichloride*, m.p. 206—207° (decomp.)], whilst $CMeCl(CH_2{\cdot}NMe_3I)_2$ or an old specimen of (**V**) yields (**VII**), the former on prolonged boiling with Ag_2O giving (**VIII**). It is concluded that (**IV**) and (**VI**) are geometrical isomerides, and that (**II**) is $NMe_2{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}NMe_2$. *Acetonyltrimethylammonium picrate* (from CH_2AcCl and aq. EtOH–NMe_3) has m.p. 149—150°. Mixed Et_2 *cis*- and *trans*-1-methyl*cyclo*propanedicarboxylate with aq. NH_3 gives the mixed *amide-NH*$_4$ salt, m.p. 167—169° (efferv., previous softening), and with N_2H_4,H_2O yields the mixed *dihydrazide*, m.p. 167—170°, which with HNO_2 affords a small amount of 2 : 3-diamino-1-methyl*cyclo*propane (*Bz*$_2$ derivative, m.p. 197—200°). Trimethyleneimine with MeI in Et_2O at 0° gives its *hydriodide*, m.p. 146·5° [resolidifying and remelting at 240—250° (decomp.)], but with MeOH–KOH, then MeI at 0°, yields N-*methyltrimethyleneimine methiodide*, m.p. 225° (decomp.).

A. Li.

III. Boiling EtI and (**I**) yield the *diethiodide*, m.p. 128°, decomp. by heat into the monohydrated dihydriodide of the Me_3 base. (**I**) and allyl iodide give the *monoallyliodide*, m.p. 145—146° (decomp.) and 207° after re-solidification (*monohydriodide*, m.p. 157—158°), converted by MeI into the *monoallyliodide monomethiodide*, m.p. 114—115° (decomp.), which appears to afford the *tetramethiodide*, m.p. >350°, of (**I**) when heated. In Et_2O (**I**) and CH_2PhI give the *dibenzyliodide monohydrate*, m.p. 128—129° (decomp.), and *monobenzyliodide*, m.p. 146—147° and 190—196° after re-solidifying (*hydriodide*, m.p. 170°). The *monobenzyliodide allyliodide* has m.p. 145—146° (decomp.). Under other conditions the reaction of the base with CH_2PhI causes rupture of the amine mol. with the formation of $NMe_2I(CH_2Ph)_2$ and the dibenzyliodide of the "pyro" base. The thermal decomp. of these products has been studied.

H. W.

Structure of sphingosine. H. E. Carter, F. J. Glick, W. P. Norris, and G. E. Phillips (*J. Biol. Chem.*, 1941, **142**, 449—450).—Sphingosine is n-$C_{12}H_{27}{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH(NH_2){\cdot}CH_2{\cdot}OH$ (cf. Klenk *et al.*, A., 1931, 829). Sphingosine sulphate and BzCl–aq. NaOH–Et_2O give the *N*-Bz derivative, reduced (PtO_2) to *N*-benzoyldihydrosphingosine (**I**), converted by BzCl–C_5H_5N into the Bz_3 derivative, m.p. 144—146° [hydrolysed by hot aq. alkali to (**I**)]. Since (**I**) is not oxidised by HIO_4, it is probably an αγ-glycol, not an αβ derivative (*loc. cit.*); (**I**), however, readily affords a cyclic acetal with PhCHO–$ZnCl_2$, a reaction characteristic of either an αβ- or αγ-glycol. A. T. P.

Quantitative investigation of amino-acids and peptides. VIII. Solubility and specific rotations of *l*(−)-leucine at 25°. M. P. Stoddard and M. S. Dunn (*J. Biol. Chem.*, 1941, **142**, 329—343).—*l*(−)-Leucine (**I**) of high purity is prepared by decomp. of the recryst. monohydrochloride, obtained from natural leucine, with aq. NH_3 at p_H 7. Solubility of (**I**) is 2·19±0·01 g. per 100 g. H_2O at 25·1±0·03°, and $[\alpha]_D^{25}$ is +15·20±0·04° in 6N-HCl, or −10·57±0·04° in H_2O; ash, H_2O, Cl, NH_3, Fe^{II}, Fe^{III}, and PO_4 content are negligible (<0·004%), methionine content is ~0·1%, and NH_2-acids other than (**I**), ~0·5%. A. T. P.

Manufacture of acetonitrile.—See B., 1942, II, 52.

II.—SUGARS AND GLUCOSIDES.

β-Form of the Cori ester (*d*-glucopyranose 1-phosphate). M. L. Wolfrom, C. S. Smith, D. E. Fletcher, and A. E. Brown (*J. Amer. Chem. Soc.*, 1942, **64**, 23—26).—$(CH_2Ph)_2$ β-*d*-glucopyranose tetra-acetate 1-phosphate (prep. described; 73% yield; cf. Zervas, A., 1939, II, 360) with H_2–PdO in abs. EtOH etc. gives β-d-*glucopyranose dibrucine* 1-*phosphate* (**I**), m.p. (+10H_2O) 160—165° (decomp.; sinters at 120—122°) and (anhyd.) 162—166° (decomp.), $[\alpha]_{5892\cdot5}^{22}$ (+10H_2O) −20° in H_2O. The isomeric α-salt (**II**) has m.p. (+8H_2O) 173—178° (sinters at 165°) and (anhyd.) 182—184° (decomp.), $[\alpha]_{5892\cdot5}^{27}$ (+8H_2O) +0·5° in H_2O. The rotatory dispersions of (**I**) and (**II**) are described. Hydrolysis of (**I**) by N-HCl at 33° is faster than that of (**II**). Derivation of cellulose from β- and of starch and glycogen from α-*d*-glucopyranose 1-phosphate makes it probable that the former exists in nature. R. S. C.

Polymorphism of *d*-galactose diethylmercaptal penta-acetate. L. H. Welsh and G. L. Keenan (*J. Amer. Chem. Soc.*, 1942, **64**, 183—186).—This substance exists in forms of initial m.p. 76·5—77°, 80·5—81°, and 90·5—91°. Photomicrographs are given.

R. S. C.

Structure of N^4-*d*-glucosidosulphanilamide. C. E. Braun, J. L. Towle, and S. H. Nichols, jun. (*J. Org. Chem.*, 1942, **7**, 19—22).—Cautious addition of β-acetobromo-*d*-glucose (**I**) in anhyd. $CHCl_3$ to a well-stirred mixture of p-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ (**II**), Ag_2O, and $CaSO_4$ in anhyd. dioxan gives *d*-glucosidosulphanilamide tetra-acetate, m.p. 191°, $[\alpha]_D^{19}$ −78·4° in anhyd. C_5H_5N, −62·6° in $CHCl_3$, deacetylated to N^4-*d*-glucosidosulphanilamide (**III**), m.p. 204° when very slowly heated, $[\alpha]_D^{23}$ −119·6° in H_2O, $[\alpha]_D^{24}$ +29·7° in 0·1N-HCl, identical with the product of Kuhn and Birkofer (A., 1938, II, 173). The conclusion that the glucose residue is attached to N^4 in (**III**) depends on the fact that it, when compared directly with (**II**) and p-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NHAc$, fails to yield a picrate, a picramide, a substituted thiocarbamide with α-$C_{10}H_7{\cdot}NC$, and fails to give a positive reaction with Ehrlich's reagent. Its mode of synthesis from (**I**) appears to justify the conclusion that (**III**) is a β-glucoside. On an equal wt. basis (**III**) is only about half as active against streptococci as (**II**) and is not less toxic. Even if the difference in mol. wts. is considered (**III**) is still slightly less active than (**II**). However, the greater solubility of (**III**) in H_2O may be advantageous.

H. W.

Acetate, m.p. 172·5—173°, of a pentahydroxychalkone hexoside from *Coreopsis gigantea*.—See A., 1942, III, 360.

Recent progress in the chemistry of pectic materials and plant gums. E. L. Hirst (*J.C.S.*, 1942, 70—78).—A review. A. Li.

***X*-Ray and electron microscope studies of the processes in the grinding of cellulose.** K. Hess, H. Kiessig, and J. Gundermann (*Z. physikal. Chem.*, 1941, **B**, **49**, 64—82).—Changes in state of cellulose (**I**) fibres by mechanical destruction have been studied. The distribution to primary fibrils of 100—750 A. thickness has been demonstrated. *X*-Ray investigations have shown that the lattice-ordered state of the fibrils disappears but reappears on treatment with H_2O not as (**I**) but as hydrated (**I**). A diminution in viscosity on grinding is attributed to processes which occur inside the primary fibrils. On continued grinding the primary fibrils become curled and matted together in clumps without any discernible fracture of the fibrils. The changes in properties of the product arise not only from surface enlargement but also from changes of state occurring inside the primary fibrils. W. R. A.

Oxidation of cellulose by nitrogen dioxide. E. C. Yackel and W. O. Kenyon (*J. Amer. Chem. Soc.*, 1942, **64**, 121—127).—Keeping cotton in N_2O_4 or circulating N_2O_4 over it gives oxidised cellulose, which is fluffy, white, non-friable, and has high affinity for basic dyes. If the CO_2H is >15%, the product is indistinguishable from the starting material. If the CO_2H is <15%, some surface hardening and shrinkage occurs. If the CO_2H is >13%, the products are sol. in 2% aq. NaOH, dil. aq. NH_3, Na_2CO_3, warm aq. C_5H_5N, or aq. quaternary NH_4 hydroxides; products containing <13% of CO_2H swell but do not dissolve. Insol. salts are obtained, *e.g.*, the Ba salt, from the hydroxide or by displacement of AcOH from acetates. CO_2H is best determined by a modification of the CO_2-evolution method used for uronic acids; displacement of AcOH from aq. $Ca(OAc)_2$ gives lower results for highly oxidised products, probably owing to incomplete penetration of the reagent or adsorption of AcOH. Interaction with N_2O_4 is at first rapid, but later much slower. Correlation of the ratio of reactants with composition of the product is good. R. S. C.

Properties of cellulose oxidised by nitrogen dioxide. I. C. C. Unwin and W. O. Kenyon (*J. Amer. Chem. Soc.*, 1942, **64**, 127—131).—Oxidation of cotton by N_2O_4 (see preceding abstract) gives oxidised cellulose (**I**) containing, after sufficiently long interaction, ~25% of CO_2H. Determination of CO_2H by (*a*) dissolution in warm aq. C_5H_5N and later addition of 0·5N-NaOH and (*b*) dissolution in aq. C_5H_5N–0·5N-NaOH, followed in both cases by back-titration, is described. Method (*a*) gives low results, similar to those of the $Ca(OAc)_2$ method; method (*b*) gives results similar to those of the CO_2-evolution method, which is considered best of all. Cu no., determined by the Forest Products Laboratory method, increases to 71·0; the Knecht–Thompson method gives much lower results; reduction of Cu salts is considered to be entirely due to fission of uronic acid units to give CHO during digestion with the

reagents. Acetates are best analysed by a distillation method. Yields of furfuraldehyde are ~60%, comparable with those from alginic and pectic acid. CO_2H and acylable OH account for all the original OH. It is concluded that oxidation by N_2O_4 attacks primary OH without affecting *sec.* OH and in fully oxidised material all CH_2·OH are converted into CO_2H. R. S. C.

New microchemical reaction for cellulose. E. E. Post and J. D. Laudermilk (*Stain Tech.*, 1942, **17**, 21—24).—3 drops of 2% I in 5% KI, diluted with 9 vols. of H_2O containing 0·28% of glycerol, are applied with a glass rod, left for 30 sec., and blotted dry. Then 1 drop of saturated aq. LiCl is added, and the prep. covered and examined. The blue colour reaction for cellulose develops within 5 min. E. E. H.

Relation between the method of preparation, distribution of substituents, and solubility in water or alkali of methyl and ethyl ethers of cellulose. J. F. Mahoney and C. B. Purves (*J. Amer. Chem. Soc.*, 1942, **64**, 15—19).—Five H_2O- or alkali-sol. methyl- and ethylcelluloses are partly esterified with *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N (heterogeneous mixtures) and the amounts of primary OH determined by conversion of the products into 6-iodides. The amounts of 2 : 3- + 3 : 4-glycol are determined by HIO_4. Alkylation in a quaternary NH_4 base gives products in which OAlk is uniformly distributed along the chain, but the technical heterogeneous alkylation of alkali-cellulose leads to non-uniform distribution; moreover, the ratio of primary to *sec.* OH alkylated is higher in the former than in the latter reaction. Steric effects probably account for this difference. R. S. C.

Methods for investigating the distribution of ethoxy-groups in a technical ethylcellulose. J. F. Mahoney and C. B. Purves (*J. Amer. Chem. Soc.*, 1942, **64**, 9—15).—Oxidation of a technical ethylcellulose (**I**) (2·48 OEt per glucose unit; mol. wt. 232) by $Pb(OAc)_4$ shows presence of 0·01 unit of 2 : 3-glycol. That of the ethylglucopyranosides (obtained by hydrolysis) by HIO_4 shows 0·25—0·29 unit of 2 : 3- + 3 : 4-glycol. That of the derived free sugars by $Pb(OAc)_4$ shows 0·13—0·15 unit of 1 : 2-glycol. Thus, 0·13—0·15 free OH per glucose unit occurs in position 2 and 0·24—0·28 in position 3. Interaction of (**I**) with *p*-$C_6H_4Me{\cdot}SO_2Cl$ (**II**) in C_5H_5N (homogeneous solution) at 20° is followed for 6 months by determination of S and OEt in the product and periodic conversion thereof into the 6-iodide by NaI in $(CH_2Ac)_2$; this shows 0·124 free primary OH per unit in (**I**). Mathematical analysis of the reaction rate (unimol.) with (**II**) shows rapid esterification of 0·151 OH per unit at $C_{(2)}$ and slower esterification of 0·245 OH at $C_{(3)}$, these estimates being more accurate than those given above. First-order consts. for reaction with (**II**) are 15, 2·3, and 0·07 for OH in positions 6, 2, and 3, respectively. R. S. C.

III.—HOMOCYCLIC.

Oxidation of *cyclo*hexane.—See B., 1942, II, 52.

Synthesis of condensed ring systems. VII. Successful use of ethylene in the Diels–Alder reaction. L. M. Joshel and L. W. Butz (*J. Amer. Chem. Soc.*, 1941, **63**, 3350—3351).—C_2H_4 with $(CH_2{\cdot}CH)_2$ at 200°/4500 lb. gives <18% of *cyclo*hexene, with $(CH_2{\cdot}CMe)_2$ at 200°/6200 lb. gives 50% of 1 : 2-dimethyl*cyclo*hexene, and with *cyclo*pentadiene at 190—200°/5800 lb. gives 74% of di*cyclo*[2 : 2 : 1]-Δ^2-heptene. R. S. C.

Preparation of $\Delta^{6:8(14)}$-, $\Delta^{7:9(11)}$-, $\Delta^{7:14}$-, and $\Delta^{8:14}$-cholestadienes. J. C. Eck and E. W. Hollingsworth (*J. Amer. Chem. Soc.*, 1942, **64**, 140—144).—Δ^8-Cholesten-7-one and $Al(OPr^\beta)_3$–$Pr^\beta OH$ give Δ^8-*cholesten-7-ol*, m.p. 79—80°, $[\alpha]_D^{24}$ +4·2° in CCl_4, dehydrated by HCl–EtOH to $\Delta^{8:8(14)}$-*cholestadiene*, m.p. 84—85°, $[\alpha]_D^{24}$ +1·1° in CCl_4 (absorption max. ~245 mμ). Δ^8-Cholestene (**I**) and $Hg(OAc)_2$–EtOH–AcOH give $\Delta^{7:9(11)}$-*cholestadiene*, m.p. 83—84°, $[\alpha]_D^{20}$ +31·3° in $CHCl_3$ (absorption max. 243 mμ.), also obtained by Br–$CHCl_3$ at −75°. With BzO_2H in $CHCl_3$, (**I**) gives $\Delta^{7:14}$-*cholestadiene*, m.p. 82—83°, $[\alpha]_D^{21}$ −93·2° in CCl_4 [absorption max. 242 and 250 mμ.; $(CH{\cdot}CO)_2O$ *adduct*, m.p. 170—174°]. $\Delta^{8(14)}$-Cholestene (**II**) and BzO_2H give $\Delta^{8:14}$-*cholestadiene*, m.p. 83—84°, $[\alpha]_D^{20}$ −23·0° in CCl_4 (absorption max. 245 mμ.), also obtained by SeO_2 in boiling EtOH (product, $[\alpha]_D^{23}$ −19·7°), Br–MeOH–Et_2O, or CrO_3, giving no $(CH{\cdot}CO)_2O$ adduct, and hydrogenatcd (Pd) to (**II**). [α] are compared with those of similar compounds. Br-titrations are discussed. R. S. C.

Catalysts for polymerisation of benzyl chloride.—See A., 1942, I, 177.

***p*-Cymene. VII. Simultaneous nitration and partial dealkylation of *p*-cymene.** T. F. Doumani and K. A. Kobe (*J. Org. Chem.*, 1942, **7**, 1—5; cf. A., 1940, II, 162).—*p*-$C_6H_4Me{\cdot}NO_2$, obtained with 1 : 4 : 2-$C_6H_3MePr^\beta{\cdot}NO_2$ by the mononitration of *p*-$C_6H_4MePr^\beta$, is derived by the replacement of Pr^β by NO_2. The spent mixed acids contain $Pr^\beta OH$ and $COMe_2$, the latter arising by oxidation of a part of the former. H. W.

Preparation and reactions of 4-amyl-*m*-xylenes. D. Nightingale and O. G. Shanholtzer (*J. Org. Chem.*, 1942, **7**, 6—14).—In the reaction between decahydronaphthalene, 4-*neopentyl*-m-*xylene*, b.p. 97—98°/10 mm., and $AlCl_3$, the neopentyl radical is cleaved to form *iso*pentane in 20% yield. This is the first primary alkyl radical to react in this manner. The branched *sec.*-amyl radical gives a larger yield of mixed pentanes in this reaction than do the two straight-chain *sec.*-amyl radicals. 5-*tert.*-Amyl-*m*-xylene (**I**), b.p. 102—103°/14 mm., obtained from *m*-xylene, $AlCl_3$, and *tert.*-$C_5H_{11}Cl$, gives the highest yield of *iso*pentane. 4-tert.-*Amyl*-m-*xylene* (**II**), m.p. 93—95°/14 mm., is derived from *m*-xylene, *tert.*-$C_5H_{11}{\cdot}OH$, and H_2SO_4. The following -m-*xylenes* are described: 4-n-*amyl*-, (**III**), b.p. 123—124°/16 mm., 4-iso*amyl* (**IV**), b.p. 116—117°/15 mm.; 4-*β*-*amyl* (**V**), b.p. 102—103°/11 mm., 4-*β*-Δ^β-*pentenyl*-, b.p. 104—113 mm.; 4-*β*-*γ*-*methylbutyl* (**VI**), b.p. 100—102°/13 mm.; 4-*β*-*γ*-*methyl*-Δ^β-*butenyl*-, b.p. 106—110°/16 mm.; 4-*γ*-n-*amyl*- (**VII**), b.p. 105—106°/13 mm.; 4-*γ*-Δ^γ-*pentenyl*-, b.p. 103—105°/16 mm.; 4-*α*-*β*-*methyl*-n-*butyl*-, b.p. 108—111°/13 mm.; 4-*α*-*β*-*methyl*-Δ^α-*butenyl*-, b.p. 107°/10 mm. They are obtained by Clemmensen reduction of the requisite ketones, of which 2 : 4-*dimethyl*isovalerophenone, b.p. 131—132°/12 mm. (*semicarbazone*, m.p. 196°), and 2 : 4-*dimethylpivalophenone*, b.p. 107—109°/6 mm., which does not yield a semicarbazone, are new. The 4-*n*- and 4-*iso*-valeryl ketones give solid *by-products*, $C_{26}H_{38}O_2$, m.p. 146° and 139—140°, respectively. *m*-Xylene is transformed by CH_2O and conc. HCl into 2 : 4-*dimethylbenzyl chloride* (**VIII**), b.p. 92—94°/8 mm.; (**I**), (**II**), and (**III**) are converted similarly into their CH_2Cl derivatives, b.p. 120—128°/3 mm., (**IX**), b.p. 115—123°/4 mm., and b.p. 125—135°/3 mm. (**X**). (**VIII**), (**IX**), and (**X**) are converted by an excess of NH_2Ac at 190—220° into the $CH_2{\cdot}NHAc$ compounds, m.p. 109°, 150°, and 105°, respectively. Nitration, reduction, and subsequent acylation of (**I**)—(**VII**) gives the $(NHAc)_2$- and $(NHBz)_2$-derivatives, m.p. 304° and 302°; — and 308°; 234° and 220°; — and 208°; 234° and 241°; 264° and 234—235°; 279—280° and 252—253°, respectively. H. W.

Poly*cyclo*hexylnaphthalenes.—See B., 1942, II, 52.

9-Vinylphenanthrenes. III. α-9-Phenanthrylstilbene. F. Bergmann (*J. Amer. Chem. Soc.*, 1942, **64**, 69—72).—α-9-Phenanthrylstilbene (**I**), m.p. 167°, prepared from *αβ*-diphenyl-α-9-phenanthrylethyl alcohol (A., 1940, II, 308), is accompanied by a small amount of an *isomeride* (**II**), m.p. 140°. (**I**) and (**II**) are shown to have the Ph in *trans*- and *cis*-positions, respectively. A trace of I in boiling $PhNO_2$ converts (**II**) into (**I**). In Et_2O, (**I**) gives a Li_2 derivative, converted by EtOH into α-9-*phenanthryldibenzyl* (**III**), m.p. 197°, and a little 9-*benzyl*-1a : 4a-*dihydro*-1 : 2 : 3 : 4-*dibenzofluorene* (**IV**), m.p. 236°, or by CO_2 into *αβ*-*diphenyl*-α-9-*phenanthrylsuccinic anhydride* (**V**), m.p. 256—258° (decomp.). In boiling Ac_2O, (**V**) gives *compounds*, $C_{29}H_{18}O_2$, m.p. 276°, and $C_{29}H_{20}O_2$, m.p. 248—249° (with CH_2N_2 gives a ? *Me* ester, m.p. 175—176°, very resistant to HI). The Li_2 derivative of (**II**) with EtOH gives (**III**) and traces of 10-*phenyl*-1 : 2 : 3 : 4-*dibenzophenanthrene* (**VI**), m.p. 185°, but with CO_2 at 0° gives (**VI**) and an amorphous acid, which gives no anhydride but in hot Ac_2O yields 2-*phenyl*-3-9′-*phenanthrylindone*, m.p. 255°, and CO_2. R. S. C.

Hydrogenation of *β*-iminonitriles. H. Adkins and G. M. Whitman (*J. Amer. Chem. Soc.*, 1942, **64**, 150—154).—$CH_2R{\cdot}CN$ (R = H, Me, Et, Pr^α, or Ph) gives, by the Thorpe reaction, $CH_2R{\cdot}C(:NH){\cdot}CHR{\cdot}CN$ or probably $CH_2R{\cdot}C(NH_2){:}CR{\cdot}CN$. Hydrogenation (Raney Ni) readily gives $CH_2R{\cdot}CH(NH_2){\cdot}CHR{\cdot}CH_2{\cdot}NH_2$ but $CH_2R{\cdot}CH(NH_2){\cdot}CHR{\cdot}CN$ could not be obtained. Except when R = Ph, a little hydrogenolysis to $NH_2{\cdot}CH(CH_2R)_2$ (not formed by way of the diamine, which is stable) occurs; if R = Ph, 2% of $Ph{\cdot}[CH_2]_2{\cdot}NH_2$ is formed. $NH{:}CBu^\alpha{\cdot}CHPr^\alpha{\cdot}CN$ exists as trimeride in freezing and as dimeride in boiling C_6H_6 and as solvate in boiling EtOH. $NPh{:}CMe{\cdot}CH_2{\cdot}CN$ (**I**) (prep. from $NH{:}CMe{\cdot}CH_2{\cdot}CN$ by NH_2Ph–AcOH–H_2O) is dimeric in boiling C_6H_6 and solvated in EtOH. $Bu^\alpha CN$ and *β*-piperidinocinnamonitrile (**II**) are monomeric in C_6H_6. Hydrogenation of (**I**) gives NH_2Ph (73—84%), $NH_2{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}NH_2$ (8%), and ? $NHBu^\alpha{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}NH{\cdot}CHMe{\cdot}CH_2{\cdot}CN$. Hydrogenation of (**II**) leads only to hydrogenolysis of the piperidino-group. Hydrogenation (Raney Ni; 70—126°/150 atm.) of $NO_2{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}COPh$ gives *βδ*-*diphenyl*-n-*butylamine*, b.p. 144·5°/1 mm. (3-*nitrophthalimide*, m.p. 129·5°; *phenylthiocarbamide*, m.p. 191—191·5°). Addition of $CH_2Ph{\cdot}CN$ and then of MeI to $NaNH_2$–Et_2O gives $CHPhMe{\cdot}CN$, converted by $CH_2Ph{\cdot}MgCl$–Et_2O into $CHPhMe{\cdot}CO{\cdot}CH_2Ph$; with NH_3–H_2–Raney Ni in dioxan at 150°/100 atm., this gives *β*-*amino*-*αγ*-*diphenylbutane*, b.p. 142·5°/51—54 mm. (*hydrochloride*, m.p. 174—175·5°; *picrate*, m.p. 190·5—191·5°; 3-*nitrophthalimide*, m.p. 152—153°; *phenylthiocarbamide*, m.p. 146·5—147°). *αγ*-*Diamino*-*β*-*methyl*-n-*pentane*, b.p. 110°/88 mm. [*platinichloride*, m.p. 237° (decomp.)], *αγ*-*diamino*-*β*-*ethyl*-n-*hexane*, b.p. 99°/17 mm. (*dihydrochloride*, m.p. 153—165°), ε-*amino*-n-*nonane*, b.p. 78°/20 mm. (*hydrochloride*, m.p. 178—180°; *picrate*, m.p. 149·5—150°), ε-*amino*-δ-*methyl*-n-*nonane*, b.p. 87—90°/18 mm. (*picrate*, m.p. 153·5—154·5°), *αγ*-*diamino*-*β*-n-*propyl*-n-*heptane*, b.p. 100°/5 mm. [*dihydrochloride*, m.p. 106—110° (decomp.)], and *αγ*-*diamino*-*βδ*-*diphenylbutane*, b.p. 166—168°/1·5 mm. (*dihydrochloride*, m.p. >280°), are incidentally prepared. R. S. C.

Hydrogenation of primary arylamines.—See B., 1942, II, 95.

Action of chlorine on arylthiocarbimides and reactions of *iso*cyanodichlorides. II. G. M. Dyson and T. Harrington (*J.C.S.*, 1942, 150—153; cf. A., 1940, II, 125).—A modified scheme is proposed for the action of Cl_2 on PhNCS; the unstable additive compound, probably NPh:C(SCl)·NPh·CSCl (cf. *loc. cit.*), is converted by NaOH into 1-anilinobenzthiazole. PhNCS–NPh:CCl_2–Cl_2 give (mainly) *p*-C_6H_4Cl·N:CCl_2, b.p. 220—226°, converted by NH_2Ph–C_6H_6 (reflux) into s-*diphenyl*-p-*chlorophenylguanidine hydrochloride*, m.p. 256° (some triphenylguanidine hydrochloride is formed). NPh:CCl_2 and $NHPh_2$ in $C_2H_2Cl_4$ yield *pentaphenylguanidine hydrochloride*, m.p. 227°; *o*-, *m*-, or *p*-C_6H_4Me·N:CCl_2 similarly gives s-*tetraphenyl*-o-, m.p. 172°, -m-, m.p. 174—176°, and -p-*tolylguanidine*, m.p. 175°, respectively. Tertiary amines do not react under the conditions. *p*-C_6H_4Me·N:CCl_2 or *p*-NO_2·C_6H_4·N:CCl_2 and EtOH (reflux) give p-*tolyl*-, m.p. 51°, or p-*nitrophenyl-urethane*, m.p. 127°, respectively, in excellent yield, whereas NPh:CCl_2 or *m*-NO_2·C_6H_4·N:CCl_2 yields the respective urethane and NH_2Ph,HCl or *m*-NO_2·C_6H_4·NH_2,HCl, respectively. *m*- or *o*-C_6H_4Me·N:CCl_2 affords the respective urethane and a *hydrochloride*, $C_{20}H_{22}O_2N_2$,HCl, m.p. 270°, or a *substance* (contains N and Cl), m.p. 108°, respectively. NPh:CCl_2 and PhOH at 150° give *Ph phenylimidocarbonate*, m.p. 136°, and similarly prepared are p-*tolyl phenyl*-, m.p. 110°, *Ph* p-*tolyl*-, m.p. 108°, p-*tolyl* o-*tolyl*-, m.p. 115°, *Ph* p-*bromophenyl*-, m.p. 154°, *Ph* p-*nitrophenyl*-, m.p. 165°, and p-*chlorophenyl* p-*nitrophenyl-imidocarbonate*, m.p. 185°. Interaction of NPh:CCl_2 with C_6H_6–$AlCl_3$ gives NHPhBz, probably through NPh:CPh·OH. A. T. P.

δ-Substituted semicarbazides. II. Semicarbazones of aldehydes and ketones. R. Barré and L. Piché (*Canad. J. Res.*, 1942, **20, B**, 17—20; cf. A., 1942, II, 88).—δ-*p*-Nitrophenylsemicarbazones are most suitable for determination of aldehydes and ketones, being very rapidly and quantitatively pptd. The following are described: δ-p-*nitrophenyl*-, m.p. 191° (*hydrochloride*, m.p. 215°), δ-2 : 4-*dinitrophenyl*-, m.p. 178°, δ-p-*nitrobenzyl*-, m.p. 164° (*hydrochloride*, m.p. 195—197°), δ-*p*-xenyl- (*hydrochloride*, m.p. 308°), and δ-4′-*nitroxenyl-semicarbazide*, m.p. 178° (*hydrochloride*, m.p. 219°); *glucose*-δ-*phenyl*-, m.p. 161°, -δ-p-*bromophenyl*-, m.p. 168°, -*benzyl*-, m.p. 115°, -p-*xenyl*- (**I**), m.p. 194°, -*nitroxenyl*-, m.p. 172°, and -*xanthyl*- (**II**), m.p. 183°, -*semicarbazone*; *acetone*-2 : 4-*dinitrophenyl*-, m.p. 248°, -p-*nitrobenzyl*-, m.p. 162°, -p-*xenyl*- (**III**), m.p. 228°, and -*nitroxenyl*-, m.p. 261°, -*semicarbazone*; *acetone*-, m.p. 264°, *benzaldehyde*-, m.p. 235—236°, m-*nitrobenzaldehyde*-, m.p. 276°, *vanillin*-, m.p. 261°, *glyoxylic acid*-, m.p. 249°, *pyruvic acid*-, m.p. 261°, and *glucose*-, m.p. 192—193°, -δ-p-*nitrophenylsemicarbazone*. Solubilities of the named and other $COMe_2$ and glucose derivatives are recorded: those of (**I**), (**II**), and (**III**) are very low, but the compounds form gels and it is difficult to dehydrate them. R. S. C.

Direct introduction of the amino- and substituted amino-groups into the aromatic and heterocyclic nucleus. VI. Action of alkali diphenylamides on aromatic nitro-compounds. F. W. Bergstrom, I. M. Granara, and V. Erickson (*J. Org. Chem.*, 1942, **7**, 98—102). —$PhNO_2$ reacts fairly readily with a solution of $NaNPh_2$ or $KNPh_2$ in liquid NH_3 at −33°, giving NPh_2·C_6H_4·NO_2-*p*, m.p. 141·4—142·6°, optimum yields (45%) being secured with an excess of $PhNO_2$. Reaction occurs also in Et_2O but is much less complete in C_6H_6. In liquid NH_3 at room temp. an unidentified product, m.p. 201—212·5°, is also obtained and this is the sole isolable product when an excess of $KNPh_2$ is used under these conditions. $Ba(NPh_2)_2$ resembles $NaNPh_2$ in its action. NHPh·C_6H_4·NO_2-*p*, m.p. 132·5—133·5°, and large amounts of tar result from KNHPh and $PhNO_2$ in liquid NH_3 at −33° whereas an unidentified material, m.p. 157—158°, is derived from KNHPh, $PhNO_2$, and KNO_3 at room temp. *o*-C_6H_4Me·NO_2 and $NaNPh_2$ give, among other products, (*o*-NO_2·C_6H_4·CH_2·)$_2$, m.p. 120—121°. Similarly, *p*-C_6H_4Me·NO_2 gives (*p*-NO_2·C_6H_4·CH_2·)$_2$, m.p. 177·5—179°, in very poor yield. $NaNPh_2$ and *m*-C_6H_4Me·NO_2 in liquid NH_3 at −33° give (?) 4-nitro-2-methyltriphenylamine, m.p. 129·5—130·5°. Definite compounds could not be obtained from $NaNPh_2$ and *o*-NO_2·C_6H_4·OMe or 1-$C_{10}H_7$·NO_2. H. W.

Identification of aromatic sulphonic acids containing an amino-group. C. F. H. Allen and G. F. Frame (*J. Org. Chem.*, 1942, **7**, 15—18).—The customary methods of identifying sulphonic acids are not applicable to those containing NH_2 on account of the sensitiveness of this group towards PCl_5 and its tendency to inner salt formation. If, however, the NH_2 is diazotised and replaced by Cl the resulting Cl-acid is readily transformed into a cryst. sulphonamide. The method is applicable to amino-mono- and -di-sulphonic acids in the C_6H_6 series and to monosulphonic acids in the $C_{10}H_8$ series. (The m.p. of chlorosulphonamides derived from the commoner aminosulphonic acids are tabulated.) In the case of disulphonic acids of the $C_{10}H_8$ series the steps are satisfactory only as far as the formation of the disulphonyl chloride by reason of the high m.p. of the disulphonamides. The disulphonyl chlorides are all solids of convenient m.p. but they do not generally crystallise well and are not suited to qual. org. analysis; 2 : 3 : 6-$C_{10}H_5Cl(SO_2Cl)_2$, m.p. 165°, is exceptional. The corresponding disulphonanilides have suitable m.p. and are readily made. 1 : 4 : 8-, 2 : 3 : 6-, 2 : 4 : 8-, 2 : 5 : 7-, and 2 : 6 : 8-$C_{10}H_5Cl(SO_2$·$NHPh)_2$ have m.p. 233°, 185°, 235°, 206°, and 192°, respectively. 1-*Chloronaphthalene*-3 : 6 : 8-*trisulphonanilide*, m.p. 249°, is described. *Chlorobenzene*-2 : 5-*disulphonamide*, m.p. 229°, and 2-*chlorotoluene*-5-*sulphonamide*, m.p. 131°, are new. H. W.

Interaction of chloramine-*T* and hydrogen sulphide, phosphine, and arsine.—See A., 1942, I, 181.

Structure of N^4-*d*-glucosidosulphanilamide.—See A., 1942, II, 166.

Acid salts of *p*-aminobenzenesulphonylguanidine.—See B., 1942, III, 86.

***p*-Acylaminobenzenesulphonylguanidine.**—See B., 1942, **II**, 142.

Manufacture of benzidine, tolidine, and dianisidine.—See B., 1942, II, 95.

Kinetic considerations of the thermal decomposition of benzenediazonium chloride in various solvents.—See A., 1942, I, 147.

Direct diazotisation of nitrobenzene. F. W. Bergstrom and J. S. Buehler (*J. Amer. Chem. Soc.*, 1942, **64**, 19—21).—$PhNO_2$ evolves N_2 when treated with $NaNH_2$ or KNH_2 in liquid NH_3 or with $Ca(NH_2)_2$ alone, but products (after hydrolysis) are tars. Addition of $PhNO_2$ to β-$C_{10}H_7$·OH (**I**) and an excess of $NaNH_2$ or KNH_2 in liquid NH_3 gives N_2 and, after hydrolysis, 13—30% of 2 : 1-OH·$C_{10}H_6$·N_2Ph; O←NPh(NH_2)·ONa and thence NPh:N·ONa are probable intermediates. Na benzene*iso*diazotate does not thus react with (**I**)–$NaNH_2$. Some, but not all, other NO_2-compounds evolve N_2 with (**I**)–$NaNH_2$, but the products were not obtained cryst. R. S. C.

Stable diazo-compounds.—See B., 1942, **II**, 143.

Preparation of tri-*m*-nitrophenyl orthoformate. M. Calvin and J. R. Segesser (*J. Amer. Chem. Soc.*, 1942, **64**, 186).—*m*-NO_2·C_6H_4·OH and CCl_3·CO_2H in conc., aq. KOH at 90° give a small amount of *tri*-m-*nitrophenyl orthoformate*, m.p. 182—183°. R. S. C.

Preparation of aryl acetoacetates.—See B., 1942, II, 95.

Influence of hydroxyl-ion concentration on the autoxidation of quinol.—See A., 1942, I, 176.

Behaviour of rhenium and of the complex thiocyanates of rhenium and molybdenum with toluene-3 : 4-dithiol.—See A., 1942, I, 181.

Course of autoxidation reactions in polyisoprenes and allied compounds. I. Structure and reactive tendencies of the peroxides of simple olefines. E. H. Farmer and A. Sundralingam (*J.C.S.*, 1942, 121—139).—*cyclo*Hexene with O_2 at 30—40° in light from a Hg-vapour lamp for 2—4 hr. yields 30—40% of oxygenated material containing 80% of Δ²-*cyclo*hexenyl H peroxide (**I**), with some Δ²-*cyclo*hexenol (**II**) and *cyclo*hexene epoxide (**III**) [isolated by reduction (Na_2SO_3) of the product immediately the O_2 intake ceases, and fractionation]. Fractionation of the oxidation product at 1 atm. yields some *trans-cyclo*hexane-1 : 2-diol. (**I**) at 70—80° gives chiefly (**II**), with a small amount of " dimeride," approx. $C_6H_{10}O_2$, but no (**III**), and with ultra-violet light at 35° followed by hydrogenation (PtO_2, EtOH) yields *cyclo*hexanol and " dimeric " material, b.p. 110—176°/0·5 mm. (**I**) with *cyclo*hexene yields (**II**), a small amount of (**III**), and polymeric material. (**I**) with N-H_2SO_4 at 40—45° during 1 week gives *cyclo*hexane-1 : 2 : 3-triol, a " dimeric " acidic residue, and small amounts of (**II**) and *cyclo*pentenecaldehyde [? from a secondary product in (**I**)]. With H_2O at 110° the same products are formed in different proportions. Hock's observations (A., 1938, II, 360) on the action of dil. NaOH on (**I**) are confirmed. 1-Methyl*cyclo*hexene with O_2 at 35° similarly yields methyl*cyclo*hexenol, 1-methyl*cyclo*hexene-1 : 2-epoxide [hydrolysed (H_2SO_4) to the *trans*-1 : 2-diol], and 2(with some 3)-*methyl*-Δ²-cyclo*hexenyl H peroxide* (**IV**), b.p. 64—67°/0·2 mm. (**IV**) is reduced (Na_2SO_3) to 2(+3)-*methyl*-Δ²-cyclo*hexenol* (*A*) [3 : 5-dinitrobenzoate, an oil (α-$C_{10}H_7$·NH_2 *complex*, m.p. 95—96°)], or (H_2, PtO_2, EtOH) to impure 2-methyl*cyclo*hexanol. (**IV**) with N-H_2SO_4 at 45° yields 1-*methyl*-cyclo*hexane*-1 : 2 : 3-*triol*, b.p. 152—154°/1 mm., m.p. 95° (40—50% yield), 1-acctyl*cyclo*pentene (5%), and crude (*A*), but no other CO-compound. (**IV**) with dil. NaOH at room temp., then at 30°, yields (*A*), and small amounts of Ac·[CH_2]$_3$·CO_2H and an *acid*, $C_7H_{10}O_2$, m.p. 207°, unaffected by H_2 (PtO_2), but oxidised ($KMnO_4$) to an acid, (?) $C_7H_{12}O_6$, m.p. 69°. 1 : 2-Dimethyl*cyclo*hexene with O_2 at 23° yields 2 : 3-*dimethyl*-Δ²-cyclo*hexenyl H peroxide* (**V**), b.p. 67—70°/0·5 mm., the 1 : 2-epoxide (hydrolysed to the *trans*-1 : 2-diol), and 2 : 3-*dimethyl*-Δ²-cyclo*hexenol* (**VI**), b.p. 80—82°/13 mm. (α-*naphthylurethane*, m.p. 139—140°), oxidised (CrO_3) to the ketone. With N-H_2SO_4 at 45°, (**V**) yields 1 : 2-*dimethyl*cyclo*hexane*-1 : 2 : 3-*triol*, m.p. 109°, impure (**VI**), some polymeric material, and 2-acetyl-1-methyl-Δ¹-*cyclo*pentene. (**V**) with dil. NaOH at room temp., then at 30—40°, yields (**VI**), Ac·[CH_2]$_3$·CO_2H, and an acid, m.p. 196—197°. With Fe^{III} phthalocyanine, (**I**) rapidly decomposes to (**II**), Δ²-*cyclo*hexenone, *cyclo*pentene-1-aldehyde, etc.; (**IV**) yields (*A*) and the corresponding ketones etc., and (**V**) yields (**VI**), the corresponding ketone, a little (CH_2·CH_2Ac)$_2$, etc. The " dimeric " products formed with (**I**), (**IV**), and (**V**) contain neutral H_2O-insol., neutral H_2O-sol., and acidic H_2O-sol. material, mostly unsaponifi-

able. The mechanism of autoxidation and reactions of the H peroxides are discussed. A. LI.

Bimolecular reduction of hindered aldehydes. R. C. Fuson, E. C. Horning, M. L. Ward, S. P. Rowland, and J. L. Marsh (*J. Amer. Chem. Soc.*, 1942, **64**, 30—33).—When RCHO is reduced by Mg + MgI_2, the primary product, $(CHR{\cdot}O{\cdot}MgI)_2$, is oxidised by R'CHO (R = R' = Ph) to COPh·CHPh·O·MgI, which gives benzoin. This oxidation does not occur if R or R' is sterically hindered and the products are then $(CHR{\cdot}OH)_2$. Thus, mesitaldehyde [prep. from *s*-$C_6H_3Me_3$ in 82·5% yield by HCl–Zn$(CN)_2$–$AlCl_3$ in $(CHCl_2)_2$ at 70°] (67 g.), m.p. 10·5°, b.p. 124—128°/15 mm., with Mg + MgI_2 in boiling C_6H_6–Et_2O gives *hydromesitoin* (13 g.), m.p. 214—215° (*diacetate*, m.p. 181—182°; also obtained from mesitoin by H_2–Cu chromite in EtOH at 125°/2300 lb.), iso*hydromesitoin* (36 g.), m.p. 160—161° [*diacetate*, m.p. 124—125°; hydrogenated (Cu chromite; abs. EtOH; 250°/2000 lb.) to (2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CH_2)_2$], and *αβ-dimesitylethylene* (1·2 g.), m.p. 132—133°. 2 : 4 : 6-*Triethylbenzaldehyde*, b.p. 146—149°/21 mm. (oxidised by air to the known acid; 2 : 4-*dinitrophenylhydrazone*, m.p. 180—181°; *semicarbazone*, m.p. 155—156°), is obtained as above in 75% yield. 2 : 4 : 6-*Tri*iso*propylbenzaldehyde* (I) (prep. as above; 65% yield), b.p. 123—125°/4 mm. (*semicarbazone*, m.p. 150—151°), with Mg + MgI_2 gives 2 : 4 : 6 : 2' : 4' : 6'-*tri*iso*propyl-hydrobenzoin* (II), m.p. 285—286° (*diacetate*, m.p. 201—202°), -iso*hydrobenzoin* (III), m.p. 186—187° (*diacetate*, m.p. 160—161°), and -*stilbene*, m.p. 147—148°. Hydrogenation (Cu chromite; EtOH; 250°/6000 lb.) of (II) or (III) gives *αβ-di*-2 : 4 : 6-*tri*iso*propylphenylethane* (IV), m.p. 160—161° (3 : 3'-Br_2-compound, m.p. 199—200°, prepared by Br–$CHCl_3$). *s*-$C_6H_3Pr^{\beta}_3$ with $CH_2Cl{\cdot}OMe$ and $SnCl_4$ in CS_2 at 0° gives 2 : 4 : 6-*tri*iso*propylbenzyl chloride* (85%), b.p. 129—130°/4 mm., which with MgMeI–Et_2O yields (IV). 2 : 3-*Dimethyl*-1-*naphthaldehyde* [*guaialdehyde*] (V) (prep. from 2 : 3-$C_{10}H_6Me_2$ as above in 38% yield with other aldehydes), m.p. 77·5—78·5°, b.p. 165—168°/4 mm. [*semicarbazone*, m.p. 265° (decomp.)], with Mg + MgI_2 gives *αβ-di*-2 : 3-*dimethyl*-1-*naphthylethylene glycol* (VI), m.p. 162—163·5° (*diacetate*, m.p. 198—199°), and an *isomeride*, m.p. 274—275·5° (*diacetate*, m.p. 290—293°), thereof. With H_2–Raney Ni in EtOH at 150°/1400 lb., followed by Pd–C at 250° on the product, (V) gives 1 : 2 : 3-$C_{10}H_5Me_3$, with H_2O_2–AcOH gives 1 : 2 : 3 : 4-O:$C_{10}H_4Me_2$:O [obtained similarly, but impure, from (VI)], and with Al$(OPr^{\beta})_3$ in C_6H_6 gives 2 : 3-*dimethyl*-1-*hydroxymethylnaphthalene* [*guaiylcarbinol*], m.p. 114—115°. R. S. C.

Cyclisation of dieninenes. XIII. Methoxy*cyclo*hexenylacetylene derivatives. C. S. Marvel and W. L. Walton (*J. Org. Chem.*, 1942, **7**, 88—97; cf. A., 1941, II, 357).—4-Methoxy*cyclo*hexanone (I), b.p. 84—85°/14 mm. (semicarbazone, m.p. 175—176·5°; 2 : 4-dinitrophenylhydrazone, m.p. 150°), is condensed with C_2H_2 in presence of K *tert.*-amyloxide to 4-*methoxy*-1-*acetylenyl*cyclo*hexanol* (II), b.p. 121—122°/20 mm. (p-*nitrobenzoate*, m.p. 74·5—75·5°; 3 : 5-*dinitrobenzoate*, m.p. 112—114°), accompanied by (?) 4 : 4'-*dimethoxy*-2-cyclo*hexylidene*cyclo*hexanone*, b.p. 155°/4 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 154—155°). (II) is reduced (H_2–PtO_2–EtOH) to 4-*methoxy*-1-*ethyl*cyclo*hexanol*, b.p. 114—116°/22 mm. (3 : 5-*dinitrobenzoate*, m.p. 117·5—118°), stereoisomeric with the *alcohol*, b.p. 114—122°/22 mm. (3 : 5-*dinitrobenzoate*, m.p. 117—118°), prepared from (I) and MgEtBr. (II) is rearranged by conc. H_2SO_4 at room temp. to a ketone (2 : 4-*dinitrophenylhydrazone*, m.p. 163—164°). Treatment of 1-acetylenyl*cyclo*hexanol with MgEtBr and then with (I) leads to *αβ*-1 : 1'-*dihydroxy*-4-*methoxydi*cyclo*hexylacetylene* (III), *cis–trans* isomerides, b.p. 110°/10^{-5} mm. (3 : 5-*dinitrobenzoate*, m.p. 166—167°), and m.p. 60—62° (3 : 5-*dinitrobenzoate*, m.p. 131—132°). Similar condensation of (II) with *cyclo*pentanone gives an (impure) *glycol* (IV), b.p. 110°/10^{-5} mm.; an analogous compound (V) is obtained from 2-methyl*cyclo*pentanone and a *glycol*, b.p. 110°/10^{-5} mm., from (I). Treatment of (III), (IV), and (V) with H_2SO_4 affords respectively $\Delta^{1'}$-cyclo*hexenyl*-, b.p. 135—135·5°/2 mm., $\Delta^{1'}$-cyclo*pentenyl*-, b.p. 174—175°/19 mm., and $\Delta^{1'}$-2-*methyl*cyclo*pentenyl*-, b.p. 137—139°/3 mm., -Δ^{1}-4-*methoxy*cyclo*hexenylacetylene*. The separation of (III) into its two components does not simplify the problem of separating the products obtained by the cyclisation reaction. This is evidence that the first step is dehydration which converts either isomeride into the same acetylene. Attempts to dehydrate (III) directly give a mixture of cyclic ketones and other products. This mixture is reduced (PtO_2–H_2) and then treated with 2 : 4-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$ to give a mixture of cryst. 2 : 4-*dinitrophenylhydrazones*. Two of these, m.p. 190—191° and 173—174°, give analytical data as required by derivatives of the expected cyclic ketone but it is uncertain whether they are stereoisomerides of the phenanthrone or whether one is a phenanthrone and the other a spiranone. The third compound, m.p. 227—228°, is dodecahydrophenanthrone-2 : 4-dinitrophenylhydrazone, proving loss of OMe as MeOH and reduction of the double linking thus developed. When the conditions of cyclisation are made more drastic, the amount of the unsubstituted ketone derivative increases at the expense of one of the methoxylated substances. Loss of OMe occurs after cyclisation since its loss at the acetylene stage would result in the formation of a dihydrobenzene derivative and thence a benzenoid mol. which does not cyclise. Dehydrogenation of the mixed ketones over Pd–C at 330° gives phenanthrene, 3-methoxyphenanthrene, and, apparently, anthracene and a methoxyanthracene. The isolation of the two hydrocarbons is an indication that at least one of the cyclisation products may be a spiran. Oxidation of 3-methoxy-*cyclo*hexanol with H_2SO_4 and $Na_2Cr_2O_7$ at 65—70° gives only Δ^{2}-*cyclo*hexenone, b.p. 63°/14 mm. (semicarbazone, m.p. 160—161°; 2 : 4-*dinitrophenylhydrazone*, m.p. 165—166° from EtOH or 167·5—168° from EtOAc). Δ^{1}-*cyclo*Hexenylacetophenone (2 : 4-*dinitrophenylhydrazone*, m.p. 163—164°) is not affected by cold AcOH–H_2SO_4 or by hot AcOH containing a little H_2SO_4 and is hydrolysed to COPhMe by fairly conc. aq. H_2SO_4. H. W.

Organic sulphur compounds. XXVII. Relation between the constitution of thioethers and thiols and their sensitivity towards alkali. A. Schönberg and Y. Iskander (*J.C.S.*, 1942, 90—95).—p-*Nitrobenzylthiolacetic acid*, m.p. 114°, obtained from $SH{\cdot}CH_2{\cdot}CO_2H$–*p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2Cl$ in aq. EtOH–$NaHCO_3$ (reflux), is hydrolysed by boiling 5% aq. NaOH for 5 min., through (probably) $ONa{\cdot}NO{:}C_6H_4{:}CH{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, to *p*-azobenzaldehyde (I). Similarly prepared is *β*-p-*nitrobenzylthiolpropionic acid*, m.p. 104—105°, hydrolysed to *p*-azoxybenzaldehyde and $(CO_2H{\cdot}[CH_2]_2{\cdot}S{\cdot})_2$ (II), with a trace of (I). *p*-$NO_2{\cdot}C_6H_4{\cdot}CPh_2Cl$ and $SH{\cdot}CH_2{\cdot}CO_2H$–PhMe give p-*nitrotriphenylmethylthiolacetic acid*, m.p. 153—155°, hydrolysed by 5% aq. NaOH to *p*-$NO_2{\cdot}C_6H_4{\cdot}CHPh_2$ (III) [probably through $OH{\cdot}NO(ONa){\cdot}C_6H_4{\cdot}CPh_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H \rightarrow ONa{\cdot}S{\cdot}CH_2{\cdot}CO_2H$ + $OH{\cdot}NO{:}C_6H_4{:}CPh_2 \rightarrow$ (III)]. p-*Aminobenzylthiolacetic acid*, m.p. 155—156°, prepared from the NO_2-compound by Sn–HCl, is unchanged after boiling with 5% aq. NaOH for 20 min.; $CH_2Ph{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, $CH_2Ph{\cdot}S{\cdot}[CH_2]_2{\cdot}CO_2H$, new m.p. 82—83°, and $CPh_3{\cdot}S{\cdot}CH_2{\cdot}CO_2H$ are affected only slightly or not at all by boiling 5% aq. NaOH. COPh·CHPhCl (IV) and NaSH–EtOH at 0° yield *didesyl sulphide*, $(COPh{\cdot}CHPh)_2S$ (V), m.p. 168—169° and 128—129° (probably *r*- and *meso*-forms), and *desylthiol*, COPh·CHPh·SH (VI), m.p. 42—44° [hydrolysed by 10% aq. NaOH–EtOH to $COPh{\cdot}CH_2Ph$ (VII)]. (IV)–BzSH–EtOH, or (VI)–BzCl–C_5H_5N, afford *desyl thiobenzoate*, m.p. 110—112°, hydrolysed to (VII), BzOH, H_2S, and S. (V) (either form) also gives (VII), with some $OH{\cdot}CPh_2{\cdot}CO_2H$. (IV) and $SH{\cdot}[CH_2]_2{\cdot}CO_2H$ at 100° (bath) yield (II) and *β-desylthiolpropionic acid*, m.p. 108—109°. Alkaline hydrolysis of the latter is slower than with desylthiolacetic acid, which readily affords (VII). (IV)–PhSH–NaOEt give COPh·CHPh·SPh, new m.p. 83—84°, only partly decomposed by boiling aq. NaOH–EtOH to PhSH. $COPh{\cdot}CPh_2Cl$ (VIII)–BzSK–EtOH afford *α-benzoylbenzhydryl thiobenzoate*, m.p. 129—130°, converted by 10% aq. NaOH–EtOH into *α-benzoylbenzhydrylthiol*, m.p. 98—101° (aq. $FeCl_3$–AcOH gives the corresponding *disulphide*, m.p. 150—154°). (VIII) and $SH{\cdot}CH_2{\cdot}CO_2H$ or $SH{\cdot}[CH_2]_2{\cdot}CO_2H$ at 100° (bath) yield $COPh{\cdot}CHPh_2$ and $COPh{\cdot}CPh_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, or (II) and *β-(benzoylbenzhydrylthiol)propionic acid*, m.p. 134—136°, respectively; hydrolysis of the respective acid by boiling 7% aq. NaOH yields benzhydrylthiolacetic acid, m.p. 128° (cf. Behaghel *et al.*, A., 1939, II, 374), and *β-(benzhydrylthiol)propionic acid*, m.p. 89—90°. (VIII) and PhSH–PhMe (boil) afford *Ph α-benzoylbenzhydryl sulphide*, m.p. 119°, converted by 10% aq. NaOH–EtOH into $CHPh_2{\cdot}SPh$. Mechanisms of the various hydrolysis reactions are discussed. There is no general parallelism between thermolability of thioethers and their sensitivity to alkali, *e.g.*, (V) is thermolabile (forms a blue thiobenzil) and is also sensitive to alkali, whilst the thermolabile $CPh_3{\cdot}SPh$ is very stable to alkali. A. T. P.

Vapour-phase esterification of benzoic acid with ethyl alcohol. Effect of oxides on the catalytic activity of silicon carbide and alundum.—See A., 1942, I, 150.

Mechanism of "aromatising" diene reactions in nitrobenzene. F. Bergmann (*J. Amer. Chem. Soc.*, 1942, **64**, 176—177).—Aromatisation during diene reactions can occur when dienolisation is possible. Thus, di*cyclo*hexenyl with $(CH{\cdot}CO)_2O$ in boiling $PhNO_2$ gives 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene-9 : 10-dicarboxylic anhydride (I), m.p. 305°, but with $CHMe{:}CH{\cdot}CO_2H$ or $CHPh{:}CH{\cdot}CO_2H$ gives 9-*methyl*-, m.p. 164°, and 9-phenyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11 : 14-dodecahydrophenanthrene-10-carboxylic acid, respectively. In boiling $PhNO_2$ 3 : 6-diphenyl-1 : 2 : 3 : 6-tetrahydrophthalic anhydride gives 3 : 6 : 1 : 2-$C_6H_2Ph_2(CO)_2O$ and in $PhNO_2$ at 170—175° 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11 : 14-dodecahydrophenanthrene-9 : 10-dicarboxylic anhydride gives (I), but anthracene*endo*succinic anhydride is unchanged. *meso*-$(CHPh{\cdot}CO_2H)_2$ in hot $PhNO_2$ gives $(CHPh{\cdot}CO)_2O$, and benzoin gives benzil. *p*-$C_6H_4Br{\cdot}NO_2$, *p*-$C_6H_4Cl{\cdot}NO_2$, or *m*-$C_6H_4(NO_2)_2$ does not cause aromatisation. R. S. C.

Chemotherapeutic comparison of the trypanocidal action of aromatic diamidines. J. N. Ashley, H. J. Barber, A. J. Ewins, G. Newbery, and A. D. H. Self (*J.C.S.*, 1942, 103—116).—Amidines are best obtained by saturating with HCl a solution of the nitrile in EtOH (2·5—3 mols.) and, for sparingly sol. aromatic nitriles, an inert diluent ($CHCl_3$, C_6H_6, $PhNO_2$, or an excess of EtOH) at 0—5°, keeping for 5—7 days at room temp., and treatment of the resulting OEt·CR:NH,HCl (*i*) with 10% NH_3–abs. EtOH. Reaction occurs between OEt·CR:NH and NH_3, but 10 mols. of NH_3 are required

to suppress the decomp., (*A*) + 2EtOH → NH_4Cl + $CR(OEt)_3$. The following are thus prepared: p-*aminophenylacetamidine dihydrochloride*, m.p. 270°; p-*amidinomethylbenzamidine dihydrochloride*, m.p. 280—285° (decomp.); 4 : 4′-diamidino-, *-dimethylamidino-*, *-di-N-diethylamidino-*, *-di-N-phenylamidino-*, and *-diamidinomethyl-diphenyl dihydrochloride*; 4 : 4′-diamidinodiphenylmethane dihydrochloride, -ethane dihydrochloride, +0·5H_2O, and *-propane dihydrochloride*; 4 : 4′-*diamidino-triphenylmethane dihydrochloride*, *-methyldiphenyl dihydrochloride*, *-benzophenone dihydrochloride*, m.p. 300°, *-benzhydrol dihydrochloride*, m.p. 212°, *-benzylideneacetophenone dihydrochloride*, *-deoxybenzoin dihydrochloride*, +1·5H_2O, m.p. 280—282°, -diphenyl ether, m.p. 215—216° (*dihydrochloride*, +2H_2O), *-diphenyl sulphide*, m.p. 209—210° (decomp.), *-diphenylsulphone dihydrochloride*, m.p. 290° (decomp.), -benzylaniline dihydrochloride, +H_2O, m.p. 296°, -dibenzylamine trihydrochloride, *-dibenzyl ether*, m.p. 195° (decomp.) (*dihydrochloride*, +H_2O), -dibenzyl sulphide, m.p. 198—199° (decomp.), *-diphenoxymethane dihydrochloride*, m.p. 249° (decomp.), -αβ-diphenoxyethane, m.p. 234—235° (decomp.) (*dihydrochloride*, +H_2O, m.p. 297°), -αγ-diphenoxypropane dihydrochloride, m.p. (+H_2O) 292° or (anhyd.) 300°, *-αδ-diphenoxybutane dihydrochloride*, +2H_2O, m.p. 259—261°, -αε-diphenoxy-*n*-pentane, m.p. 186° (decomp.) [*dihydrochloride*, +2H_2O, m.p. 233—234° (decomp.); *dimethanesulphonate*], *-aζ-diphenoxy-n-hexane dihydrochloride*, +2H_2O, m.p. 246—247° (decomp.), *-aη-diphenoxy-n-heptane*, m.p. 175—177° (decomp.) [*dihydrochloride*, +2H_2O, m.p. 245—246° (decomp.)] -aκ-diphenoxy-*n*-decane dihydrochloride, m.p. 254°, *-azobenzene dihydrochloride*, +H_2O, m.p. >300°, *-benzanilide*, m.p. 245—250° (decomp.), *-benzenesulphonanilide dihydrochloride*, +4H_2O, m.p. 239°, *-β*-phenoxyethylaniline, m.p. 204° (decomp.) (dihydrochloride, +2H_2O, m.p. 296—297°), *-diphenyl disulphide dihydrochloride*, +2H_2O, m.p. >300°, *-diphenylcarbamide dimethanesulphonate*, +H_2O, and *-αδ-diphenylbutadiene dihydrochloride*; *di*-(p-*amidinophenylmethyl*) *ether*, m.p. indefinite (*dihydrochloride*); 4-*amidino-2′-cyanodiphenyl*, m.p. 160—161°; 3 : 4′-, m.p. 300°, and 4 : 4′-diamidinostilbene dihydrochloride, +2H_2O, m.p. 300°, and anhyd. (corresponding *dimethanesulphonate*); 4-*nitro-*, m.p. 300°, reduced by $SnCl_2$–aq. HCl–AcOH to 4-*amino-4′-amidinostilbene dihydrochloride*, m.p. 300°; 4-*amidinodiphenyl ether*, m.p. 126—127°; *p*-amidinophenyl *p*-amidinobenzyl ether, m.p. 232—233° (*dihydrochloride*); m-*amidinophenyl p-amidinobenzyl ether dihydrochloride*, +0·5H_2O; p-*amidinomethylphenyl* p-*amidinobenzyl ether*, m.p. 182°; p-*amidinophenyl β*-p-*amidinophenylethyl ether dihydrochloride*, +H_2O; *aγ-di*-m-*amidinophenoxypropane dihydrochloride*, m.p. 202—204° (decomp.); *aε-di*-m-*amidinophenoxy-n-pentane dihydrochloride*, +2H_2O; *ωω′-di*-p-*amidinophenoxyxylene dihydrochloride*, +H_2O; and p-*di-p′-amidinobenzyloxybenzene dihydrochloride*, +2H_2O. Yields of dinitriles obtained by the Sandmeyer reaction are much improved by sublimation of the crude product at 0·1—1 mm. (apparatus described). Thus are prepared 4 : 4′-*dicyano-triphenylmethane* (5%), m.p. 134—145°, *-benzophenone* (I) (60%), m.p. 162° (lit. 204°) (*phenylhydrazone*, m.p. 242—243°), *-benzhydrol* [prep. from (I) by Al–Hg in EtOH–NH_3], m.p. 158—159°, *-stilbene* (II) (45%), m.p. 282°, *-azobenzene* (45%), m.p. 270°, and *-diphenyl sulphide*, m.p. 133—134°. The di-(imino-ether) from (II) with NHPh·NH_2 in abs. EtOH at 50° gives *αβ-di*-(p-*phenylbenzamidrazino*)*ethylene*, m.p. 261—262° (decomp.) (*dihydrochloride*, m.p. >300°). 3 : 4′-Diaminostilbene, m.p. 153°, is obtained from the $(NO_2)_2$-compound by $SnCl_2$–AcOH–aq. HCl, and converted (Sandmeyer) into 3 : 4′-*dicyanostilbene* (26%), m.p. 137—138°. Addition of Ac_2O to *p*-NO_2·C_6H_4·CH_2·CO_2Na and *p*-NO_2·C_6H_4·CH:CH·CHO at 140—150° and heating at 150° and then with more Ac_2O at 160° gives *αδ-di*-p-*nitrophenyl-*$\Delta^{\alpha\gamma}$*-pentadienoic acid*, m.p. 295—300°, reduced by $SnCl_2$–aq. HCl–AcOH to the $(NH_2)_2$-acid, which yields (Sandmeyer) *αδ-di*-p-*cyanophenylbutadiene*, m.p. 260—261° (decomp.). 4-*Cyanostilbene*, m.p. 114°, is prepared (Sandmeyer) in 16% yield. *p*-NO_2·C_6H_4·CH_2·CO_2H and *p*-NHAc·C_6H_4·CHO in piperidine at 160° give 4-*nitro-4′-acetamido-*, m.p. 255°, hydrolysed (aq. EtOH–HCl) to 4-nitro-4′-amino-, m.p. 245° (lit. 229—230°), which affords 4-*nitro-4′-cyano-stilbene* (31%), m.p. 247—249°. $(CH_2·C_6H_4·CH:N·OH-p)_2$ in boiling Ac_2O gives 70% of $(p\text{-}CN·C_6H_4·CH_2)_2$, other methods giving poor yields. $(p\text{-}NH_2·C_6H_4·N:)_2$, m.p. 245—246°, is best obtained by reducing the $(NO_2)_2$-compound by Na_2S in boiling aq. EtOH. Distillation of $(CH_2Ph·CO_2)_2Ca$ in a steel retort gives 60% of $CO(CH_2Ph)_2$, b.p. 178—182°/10—11 mm., reduced (Clemmensen) to Ph·$[CH_2]_3$·Ph (70%), b.p. 155—160°/9—10 mm., which affords successively *αγ-di*-p-*chloromethyl-*, m.p. 103—104°, *-hydroxymethyl-*, m.p. 118—122°, -aldehydo-, an oil (dioxime, m.p. 125—127°), and *-cyano-phenylpropane*, m.p. 94—95°. *p*-CN·C_6H_4·CHO (III), *p*-CN·C_6H_4·COMe, and a little piperidine in boiling, abs. EtOH give 4 : 4′-*dicyanobenzylideneacetophenone*, m.p. 216—217°, obtained less well by other methods and resistant to H_2–Pd. *Di*-p-*cyanophenyl ether*, m.p. 180°, is obtained in 50% yield by the Sandmeyer reaction and in 37% yield from *p*-CN·C_6H_4·ONa (IV), *p*-C_6H_4BrCN (V), and a little Cu powder at 250—270°. Heating *di*-p-*carbamylphenylsulphone* (prep. from the acid by way of the acid chloride), m.p. >300°, with P_2O_5 gives *di*-p-*cyanophenylsulphone*, m.p. 232—233°, also obtained by the Sandmeyer reaction. Boiling (V) with PhOH (excess) and KOH gives *Ph* p-*cyano-*, m.p. 43—45°, and p-*carbamyl-phenyl ether*, m.p. 164—165°. *p*-$NH_2·C_6H_4·CN$ (VI), m.p. 82—84°, is best (80%) obtained by boiling crude *p*-NHAc·C_6H_4·CH:N·OH in Ac_2O and hydrolysing (2N-HCl) the product. The Sandmeyer reaction [$KCu(CN)_2$; 90—95°] gives 65—70% of *p*-OH·C_6H_4·CN, b.p. 148°/1 mm., which with NaOEt and then *p*-CN·$C_6H_4·CH_2Cl$ (VII) in boiling EtOH gives 90% of p-*cyanophenyl* p-*cyanobenzyl ether*, m.p. 167—168°. With *m*-OH·C_6H_4·CN, *p*-OH·$C_6H_4·CH_2$·CN, or *p*-$C_6H_4(OH)_2$, (VII) gives similarly m-*cyanophenyl*, m.p. 97—98°, *ω-cyano-p-tolyl* p-*cyanobenzyl ether* (and a little amide), m.p. 92°, and 1 : 4-*di*-p-*cyanobenzyloxybenzene*, m.p. 170—171°, respectively. CH_2I_2 or Br·$[CH_2]_n$·Br (*n* = >1) with (IV) (prep. by NaOEt– or NaOH–EtOH) in boiling, abs. EtOH gives *di*-p-*cyanophenoxymethane* (30%), m.p. 148°, *αβ-di*-p-*cyanophenoxyethane* (VIII) (55%), m.p. 197°, *aγ-di*-p-*cyanophenoxypropane* (83%), m.p. 188°, *aδ-di*-p-*cyanophenoxy-n-butane* (60%), m.p. 168—169°, *aε-di*-p-*cyanophenoxy-n-pentane* (78%), m.p. 114—114·5°, *aζ-di*-p-*cyanophenoxy-n-hexane* (70%), m.p. 147°, *aη-di*-p-*cyanophenoxy-n-heptane* (55%), m.p. 107°, and *aκ-di*-p-*cyanophenoxy-n-decane* (30%), m.p. 123°; *p*-$C_6H_4(CH_2Br)_2$ gives similarly *ωω′-di*-p-*cyanophenoxyxylene* (60%), m.p. 215—216°; a similar reaction in H_2O gives *β*-p-*cyanophenoxyethyl bromide* [45%; and a little (VIII)], m.p. 59°, which with (VI) at 130—140° gives 4 : 4′-*dicyano-β-phenoxyethylaniline* (35%), m.p. 163°. Hydrolysis of (VII) by aq. Na_2CO_3 gives successively 4-cyano- (IX), m.p. 41—42°, b.p. 203°/53 mm. (*phenylurethane*, m.p. 112—113°), and 4-*carbamyl-benzyl alcohol*, m.p. 134—135° [believed by Banse (A., 1894, i, 575) to be (IX)], but in boiling 33% aq. KOH gives $(p\text{-}CO_2H·C_6H_4·CH_2)_2O$, m.p. 272—274° (and some *p*-OH·$CH_2·C_6H_4·CO_2H$), converted by PCl_5 into the diacid chloride and thence successively by aq. NH_3 into *di*-p-*carbamyl-*, m.p. 241°, and by P_2O_5 in xylene into *di*-p-*cyano-benzyl ether*, m.p. 97—98°, also obtained from (VII), (IX), and NaOEt in EtOH at 95—100°. With N_2O_4–$CHCl_3$ at 0° and later room temp., (IX) gives (III) and a little acid, but with $Cu(NO_3)_2$ gives mixtures. With KCN–EtOH–H_2O, (III) gives 4 : 4′-*dicyanodeoxybenzoin* (40%), m.p. 219—220°, and a little acid. p-*Cyanobenzoyl chloride* (prep. by $SOCl_2$; PCl_5 gives too much anhydride), m.p. 65°, with (VI) in C_5H_5N gives p-*cyanobenz-p′-cyanoanilide*, m.p. 259—261°; p-*cyanobenzenesulphon-p′-cyanoanilide*, m.p. 201—202°, is similarly prepared. Ph·$[CH_2]_2$·Br (X) (prep. simplified; 90% yield) and (IV) give p-*cyanophenyl β-phenylethyl ether* (20%), m.p. 64°, which with HNO_3–H_2SO_4 at −5° gives 3 : 4 : 1-$NO_2·C_6H_3(OH)·CN$, m.p. 143°, but with HNO_3 (*d* 1·5) at −10° to 0° gives 2-*nitro-4-cyanophenyl β-*(? 4-)*nitrophenylethyl ether*, m.p. 185—186°, hydrolysed by conc. H_2SO_4 at 90° to 3 : 4 : 1-$NO_2·C_6H_3(OH)·CO_2H$ (42%). Only traces of ether are obtained from *p*-OH·C_6H_4·CN and *p*-$NO_2·C_6H_4·[CH_2]_2$·Br (XI). *β*-p-*Aminophenylethyl bromide hydrochloride*, m.p. 212—213°, is obtained from (XI) by H_2–PtO_2 in HCl–EtOH or by $SnCl_2$–HCl at 80—90° and gives (Sandmeyer; 20—30°; in presence of C_6H_6; 40% yield) *β*-p-*cyanophenylethyl bromide*, m.p. 53°, b.p. 135—140°/2 mm., and thence p-*cyanophenyl β*-p-*cyanophenylethyl ether* (10—12%), m.p. 129—130°. *p*-CN·C_6H_4·NHBz and PCl_5 at 120° give N-p-*cyanophenylbenziminochloride* (76%), m.p. 88—89°, b.p. 194—198°/3 mm., which with (IV) in Et_2O gives N-p-*cyanophenylbenzimino-p′-cyanophenyl ether* (82%), m.p. 155°, rearranged smoothly at 280—300° into *benzdi*-p-*cyanophenylamide* (XII), m.p. 219°. This gives *benzdi*-p-*amidinophenylamide*, +2·5H_2O, m.p. 194° (decomp.), converted, after dehydration (100—110°/1—2 mm.), at 180—200° into NH_2Bz (82%) and *di*-p-*cyanophenylamine* (76%), m.p. 240—246° [obtained by hydrolysis of (XII) in $(CH_2·OH)_2$, but not from (V) and (VI)], which yields *di*-p-*amidinophenylamine dihydrochloride*, +H_2O, or its *H sulphate*, *B*,1·5H_2SO_4. R. S. C.

Physico-chemical properties of the chromophoric groups, azomethine (·CH:N·) and azomethinevinylene (·CH:CH·CH:N·).—See A., 1942, I, 164.

Derivatives of *β-o*-anisylpropaldehyde. A. Zaki and H. Fahim (*J.C.S.*, 1942, 182).—*β-o*-Anisylpropaldehyde (prep. from the acid chloride by H_2–Pd in xylene) gives a $NaHSO_3$ compound, m.p. 163—164°, and a p-*nitrophenylhydrazone*, m.p. 126—127°. F. R. S.

Catalytic action of Japanese acid earth. XI. Isomerisation of aldehydes to ketones and the explanation of migration of radicals on the electronic viewpoint (continued). K. Ishimura (*Bull. Chem. Soc. Japan*, 1941, **16**, 252—262; cf. A., 1942, II, 55).—*p*-$C_6H_4Me·MgI$–$CH_2Bz·OH$–Et_2O afford di-*p*-tolyl, *p*-C_6H_4MeI, PhMe, and *α-phenyl-α-*p-*tolylethylene glycol* (I), m.p. 84·5—85·5° [*monobenzoate*, m.p. 136° (corr.)], oxidised by CrO_3–AcOH to *p*-$C_6H_4Me·COPh$. (I) and dil. H_2SO_4 at 180—185° afford *p*-$C_6H_4Me·CHPh·CHO$, b.p. 176° (corr.)/7 mm., which, passed over Japanese acid earth at 300—350°, gives C_6H_6, PhMe, and $COPh·CH_2·C_6H_4Me$-*p* (*p*-$C_6H_4Me·CO·CH_2Ph$ not formed). *p*-Toluoylcarbinol (II) and *m*-$C_6H_4Me·MgI$ yield *α-m-tolyl-α-p-tolylethylene glycol*, m.p. 59—60° [*monobenzoate* (+H_2O), m.p. 173—174° (corr.; decomp.)], oxidised to *m*-tolyl *p*-tolyl ketone (III), m.p. 72°, or converted by aq. $H_2C_2O_4$ at 115—120° into *m-tolyl-p-tolylacetaldehyde* (IV), b.p. 182° (corr.)/7 mm. [*semicarbazone*, m.p. 179—180° (corr.; decomp.)]. (IV) and aq. $AgNO_3$–KOH–EtOH yield *m-tolyl-*p-*tolylacetic acid*, m.p. 93—94°, and (III). (III) affords isomeric oximes, m.p. 119—121° and m.p. 133—134°, and Beckmann

rearrangement (PCl_5–Et_2O) yields *p*-tolu-*m*- and *m*-tolu-*p*-toluidide, respectively. *m*-$C_6H_4Me{\cdot}CH_2{\cdot}COCl$ and PhMe–$AlCl_3$ yield p-*tolyl* m-*methylbenzyl ketone* (**V**), m.p. 68° [*semicarbazone*, m.p. 192—194° (slight decomp.); *oxime*, m.p. 108—109°]. m-*Tolyl* p-*methylbenzyl ketone* (**VI**), m.p. 40—41° (oxidised on long keeping in air to *m*- + *p*-toluic acid; *oxime*, m.p. 88·5°, rearranged to p-*tolylacet*-m-*toluidide*, m.p. 123—124°), is obtained from *p*-$C_6H_4Me{\cdot}CH_2{\cdot}CN$–*m*-$C_6H_4Me{\cdot}MgI$, or from *p*-$C_6H_4Me{\cdot}CH_2{\cdot}CHO$ (**VII**)–*m*-$C_6H_4Me{\cdot}MgI$, followed by oxidation (CrO_3–AcOH) of the carbinol. (**II**) is hydrogenated (colloidal Pt; aq. AcOH) at 22°/761 mm. to p-*tolylethylene glycol*, m.p. 76·5—77·5°, converted by very dil. HCl at 180—185° into (**VII**). m-*Tolu*-p-*methylbenzylamide* has m.p. 116°. (**IV**) passed over Japanese acid earth at 300—350°/30 mm. (CO_2) yields (**VI**), but not (**V**), *i.e.*, only the *m*-tolyl radical migrates. A. T. P.

Syntheses in the carotenoid series. III. Preparation of a methyl homologue of dehydro-β-*cyclo*citral. IV. Preparation of ω-phenyl- and ω-furyl-polyenealdehydes. J. Schmitt (*Annalen*, 1941, **547**, 256—270, 270—284; cf. A., 1942, II, 126).—III. *iso*Phorone and MgMeBr give 1 : 1 : 3 : 5-tetramethyl-$\Delta^{2:4}$-*cyclo*hexadiene (**I**), b.p. 155°/760 mm., 52°/20 mm., and a small amount of a *substance*, $C_{19}H_{32}O_2$, m.p. 162·5°. With $(CH{\cdot}CO)_2O$, (**I**) gives an *adduct*, m.p. 101° (derived acid, m.p. 100°), with Br gives 1 : 2 : 3 : 5 : 4 : 6-$C_6Me_4Br_2$, and with SeO_2 in aq. AcOH gives 2 : 2 : 4 : 6-tetramethyl-$\Delta^{3:5}$-*cyclo*hexadienone (**II**), b.p. 90—95°/16 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 234°), *iso*durene, and ? 2 : 2 : 4-*trimethyl*-6-*hydroxymethyl*-$\Delta^{3:5}$-cyclo*hexadienone*, b.p. 86—87°/0·3 mm. (absorption max. 258 ± 1 mμ.; gives a 2 : 4-*dinitrophenylhydrazone*, $C_{16}H_{16}O_4N_4$, m.p. 237°, and *semicarbazone*, $C_{11}H_{15}ON_3$, m.p. 206°, with loss of H_2O). With a drop of H_2SO_4 in Ac_2O, (**II**) gives a red and with $SbCl_3$–$CHCl_3$ a bluish-green colour, with $(CH{\cdot}CO)_2O$ gives an *adduct*, m.p. 152° [derived acid, m.p. 172° (decomp.) (2 : 4-dinitrophenylhydrazone, m.p. 268°)]. $CH_2Br{\cdot}CO_2Et$, (**II**), and Zn in C_6H_6 give *Et* 1 : 5- (or 1 : 3-)*epoxy*-2 : 2 : 4 : 6-*tetramethyl*-Δ^3- (or Δ^5-)cyclo*hexenylacetate*, b.p. 100—105°/0·1 mm., hydrolysed by hot KOH–MeOH to an oily acid, which, when distilled at 12 mm., decomposes to give 2 : 3 : 4 : 4 : 6- or 2 : 2 : 3 : 4 : 6-pentamethyl-Δ^5-*cyclo*hexenone, b.p. 90—95°/12 mm. (*semicarbazone*, m.p. 173°), and a little ? 1 : 3 : 5 : 5-tetramethyl-6-methylene-$\Delta^{1:3}$-*cyclo*hexadiene, b.p. 70—75°/12 mm. (blue, later green, colour with $SbCl_3$–$CHCl_3$, red with a drop of H_2SO_4 in Ac_2O). With $CH_2Cl{\cdot}CO_2Et$ and NaOEt in Et_2O, (**II**) gives *Et* 1 : α-*epoxy*-2 : 2 : 4 : 6-*tetramethyl*-$\Delta^{3:5}$-cyclo*hexadienylacetate*, b.p. 105°/0·1 mm., which yields an oily acid, converted by distillation at 12 mm. into 2 : 2 : 4 : 6-tetramethyl-$\Delta^{4:6}$-*cyclo*hexadiene-1-aldehyde [*semicarbazone*, ? *forms*, m.p. 175° and (after sintering) 207° (absorption max. 307 mμ., log ε 4·27 ± 0·03); 2 : 4-*dinitrophenylhydrazone*, m.p. 200°; blue colour with H_2SO_4–Ac_2O, reddish-brown with H_2SO_4, violet after some min. with $SbCl_3$–$CHCl_3$, yellow with Schiff's reagent; reduces NH_3–$AgNO_3$], and a *substance*, $C_{12}H_{14}O_2$, m.p. 138°.

IV. ω-Phenyl- and ω-furyl-polyenealdehydes, $R{\cdot}[CH{:}CH]_n{\cdot}CHO$ (R = Ph, 2-furyl), are obtained in good yield by condensing aldehydes by piperidine acetate in a solvent (70% EtOH) in which the products are insol.; condensation with crotonaldehyde (**III**) is the easier the more unsaturated is the other reactant. Purification is by recrystallising and sublimation. Thus, $CHPh{:}CH{\cdot}CHO$ and (**III**) give ζ-phenylheptatrienal (50%), m.p. 116° (lit., 96°, 94°, 112·5—113°), and κ-phenylundecapentaenal (**IV**) (20%), m.p. 183°. $Ph{\cdot}[CH{:}CH]_2{\cdot}CHO$ and (**III**) give similar yields of *θ-phenylnonatrienal*, m.p. 144°, and *μ-phenyltridecahexaenal*, m.p. 213°. β-2-Furylacraldehyde and (**III**) give ζ-2-furylheptatrienal, m.p. 111°, and *κ-furylundecapentaenal* (**V**), m.p. 194°. δ-Furylpentadienal and (**III**) give *θ-furylnonatetraenal*, m.p. 155°, and *μ-furyltridecahexaenal*, m.p. 218°. In C_6H_6, (**IV**) and (**III**) give ξ-phenylpentadecaheptaenal (80%), m.p. 232° (lit. 234°). In PhMe, (**V**) and (**III**) give *ξ-furylpentadecaheptaenal* (poor yield), m.p. 230° (decomp.). The pure products are stable. Regularities of the m.p., colour, and colour reactions are noted. The Ph and furyl series are similar in properties. R. S. C.

Prototropio changes of carbonyl compounds.—See A., 1942, I, 149.

Lignin and related compounds. LIX. Aromatic aldehydes from plant materials.—See A., 1942, III, 360.

Structure and absorption spectra. IV. αβ-Unsaturated ketones.—See A., 1942, II, 164.

Application of Fries reaction to esters of quinol. R. Y. Shahane (*Current Sci.*, 1941, **10**, 523—524).—*p*-$C_6H_4(OAc)_2$ is converted by heated $AlCl_3$ into 1 : 2 : 5-$C_6H_3Ac(OH)_2$, m.p. 202°, in 76% yield. Similarly a 42% yield of 1 : 2 : 5-$C_6H_3Bz(OH)_2$ is derived from *p*-$C_6H_4(OBz)_2$. H. W.

Fries migration of the esters of polyhydroxy-phenols. R. D. Desai and C. K. Mavani (*Current Sci.*, 1941, **10**, 524).—*p*-$C_6H_4(OAc)_2$ and *p*-$C_6H_4(OBz)_2$ give good yields of 1 : 2 : 5-$C_6H_3Ac(OH)_2$ and -$C_6H_3Bz(OH)_2$. 1 : 3 : 5-$C_6H_3Me(OAc)_2$ gives 2 : 4-diacetylorcinol, readily de-acetylated to γ-orcacetophenone. 1 : 2 : 3-$C_6H_3(OAc)_3$ gives exclusively gallacetophenone in excellent yield. 1 : 3 : 5-$C_6H_3(OAc)_3$ gives mainly 2 : 4 : 6-triacetyl- or 2 : 4-diacetyl-phloroglucinol according to conditions and phloracetophenone only in traces. H. W.

***p*-Anisyl γ-phenoxypropyl ketone.** W. E. Bachmann and A. L. Wilds (*J. Amer. Chem. Soc.*, 1942, **64**, 186).—This *substance*, m.p. 59—60·5°, is obtained from *p*-$OMe{\cdot}C_6H_4{\cdot}MgBr$ and $OPh{\cdot}[CH_2]_3{\cdot}CN$ in Et_2O by way of the imine hydrochloride. R. S. C.

Application of the Nencki reaction to β-naphthol. R. D. Desai and W. S. Waravdekar (*Current Sci.*, 1941, **10**, 524—525).—Excellent yields of 1-lauryl-, 1-palmityl-, and 1-stearyl-2-naphthol are obtained from β-$C_{10}H_7{\cdot}OH$ and the requisite acid by the Nencki reaction. H. W.

Photochemical decomposition of cyclic ketones.—See A., 1942, I, 151.

Structure of vinyl polymerides.—See A., 1942, II, 164.

Synthesis of an analogue of the sex hormones. W. E Bachmann and D. G. Thomas (*J. Amer. Chem. Soc.*, 1942, **64**, 94—97).—*m*-$OMe{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}OH$ [prep. from *m*-$C_6H_4I{\cdot}OMe$, EtBr, Mg, and $(CH_2)_2O$ in Et_2O–C_6H_6; 85% yield] with PBr_3–C_6H_6 gives the bromide (66%), which with $CHNa(CO_2Et)_2$ etc. gives γ-*m*-anisylbutyric acid. The derived (PCl_5–C_6H_6) chloride with $SnCl_4$–C_6H_6 at 0° gives 1-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 78—79·5° (lit. 77·5—82°), converted by $Me_2C_2O_4$ etc. at 5—15° into the *Me* 2-*glyoxylate* (95%), m.p. 76·5—77·5°, which with glass powder at 175—185° gives *Me* 1-*keto*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoate*, m.p. 88—89·5° after sintering (Pyrex; preheated bath). Subsequent reactions are as described earlier (A., 1941, II, 138). Methylation gives *Me* 1-*keto*-6-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoate* (84%), m.p. 91—92·5°, converted (Reformatsky; dehydration; reduction; esterification) into *Me* 2-*carbomethoxy*-6-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetate*, α-, m.p. 77·5—79°, and β-form, an oil. Hydrolysis gives 2-*carbomethoxy*-6-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetic acid*, α-, m.p. 118·5—120·5°, and *β-form*, m.p. 128—130°, which by Arndt–Eistert–Wolff reactions yield *Me* β-2-*carbomethoxy*-6-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylpropionate*, α-, m.p. 52—53·5° (clear at ~64°), and β-form, an oil. Cyclisation then affords 3′-*keto*-4′-*carbomethoxy*-6-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*cyclo*pentano*-1′ : 2′-1 : 2-*naphthalene*, α-, m.p. 94—96·5°, and *β-form*, m.p. 117—119° (both m.p. after sintering; Pyrex; preheated bath), hydrolysed to 3′-*keto*-6-*methoxy*-, α-, m.p. 38·5—40·5°, and *β-form*, m.p. 112—113·5°, which with AcOH–48% HBr–N_2 gives 3′-*keto*-6-*hydroxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*cyclo*pentano*-1′ : 2′-1 : 2-*naphthalene*, α- (**I**), m.p. 155—156°, and *β-form* (**II**), m.p. 212—214° (vac.). In 5-mg. doses (**I**) is inactive, but (**II**) induces œstrous response (rats). R. S. C.

Action of hydrogen bromide in acetic acid on unsaturated 1 : 4-diketones. M. Couper and R. E. Lutz (*J. Org. Chem.*, 1942, **7**, 79—87; cf. A., 1933, 607).—The reaction between HBr–AcOH and two of four unsaturated αδ-diaryl-βγ-dimethyl-αδ-diketones is essentially reduction, whereas in the other two it is reduction and bromination in a *para* position in Ph. β-$C_{10}H_7{\cdot}OH$ acts as Br acceptor and in its presence the reactions are confined to reduction (and furanisation in two cases). A mechanism of bromination is given. The product of the action of HBr–AcOH on $(CMeBz)_2$ is trans-β-*benzoyl*-γ-p-*bromobenzoylbutane* (**I**), m.p. 125°, also obtained by reduction ($SnCl_2$, AcOH, conc. HCl) of the -Δβ-*butene* (**II**), m.p. 125° (prep. from β-*p*-bromobenzoyl-αβ-dimethylacrylyl chloride, $AlCl_3$, and C_6H_6). Dimethylfumaryl chloride, $AlCl_3$, and PhBr in CS_2 afford trans-βγ-*di*-p-*bromobenzoyl*-Δβ-*butene* (**III**), m.p. 172·5—173°, converted by $SnCl_2$ in boiling AcOH–conc. HCl or by Zn dust and boiling, conc. AcOH into 2 : 5-*di*-p-*bromophenyl*-3 : 4-*dimethylfuran* (**III**), m.p. 181°, also obtained in poor yield from PBr_5 and 2 : 5-diphenyl-3 : 4-dimethylfuran or (**I**). (**IV**) is oxidised by HNO_3 in well-cooled $EtCO_2H$ to cis-βγ-*di*-p-*bromobenzoyl*-Δβ-*butene* (**V**), m.p. 138—139°. (**I**) is scarcely affected by prolonged boiling with KOH–EtOH, is not reduced by Zn–AcOH or catalytically in presence of Pt or Pd–$BaSO_4$, and is oxidised (hot HNO_3 or $KMnO_4$) to *p*-$C_6H_4Br{\cdot}CO_2H$. It cannot readily be furanised. Bromination (Br–HBr–AcOH) of it leads to (**IV**). HBr–AcOH and $(CMeBz)_2$ in presence of β-$C_{10}H_7{\cdot}OH$ afford 2 : 5-diphenyl-3 : 4-dimethylfuran, m.p. 116—117°. (**II**) and HBr–AcOH give (**IV**) and (**I**) (ratio 1 : 4), whereas in presence of β-$C_{10}H_7{\cdot}OH$ the product is (**I**). (**III**) similarly yields (**IV**), also in presence of β-$C_{10}H_7{\cdot}OH$; (**IV**) is also obtained from (**V**). $(CH_2Bz)_2$ and HBr–AcOH give diphenylfuran, m.p. 90—92°. αβ-Dimesitoylethylene, HBr–AcOH, and β-$C_{10}H_7{\cdot}OH$ afford αδ-dimesitylbutane-αδ-dione, m.p. 130—132°. H. W.

Application of the *p*-hydrogen method to some problems of organic constitutions. I.—See A., 1942, I, 166.

Preparation of tetrahydroxybenzoquinone and rhodizonic acid salts from the product of oxidation of inositol by nitric acid. P. W. Preisler and L. Berger (*J. Amer. Chem. Soc.*, 1942, **64**, 67—69).—Prep. of K_2 rhodizonate (**I**) and of 1 : 2 : 3 : 5 : 6 : 4-$O{:}C(OH)_4{:}O$ and its K_2 salt from inositol is improved. The K salts are distinguished by solubilities in H_2O and N-HCl and analysed by potentiometric titration [$Na_2S_2O_4$; $K_3Fe(CN)_6$]. The colour changes during titration of SO_4'' by $Ba^{··}$ are probably due to (**I**). R. S. C.

Dyes related to toluidine-green. C. F. H. Allen, G. F. Frame, and C. V. Wilson (*J. Org. Chem.*, 1942, **7**, 63—67).—Comparison of the absorption spectra of homologues of toluidine-green (**I**) with those of the parent substance shows that the curves of dyes having substituents in the 6 : 7-positions resemble the unsubstituted alizarine-cyanine-green rather than (**I**). Halogen and OH in the α-position have a much greater effect on the absorption curves of this type of dye than the same group in a β-position. The 3′-sulphonic acid resembles the corresponding isomeride in the 1 : 5- (blue) series, the curve falling off in the far red. 3 : 6 : 1 : 2-$C_6H_2Cl_2(CO)_2O$, *o*-$C_6H_4Cl_2$, and $AlCl_3$ at 95—98° yield 3 : 6-*dichloro*-o-3′ : 4′-*dichlorobenzoylbenzoic acid*, m.p. 170—171° after softening at ~164°, cyclised by ~8% oleum at 160° to 1 : 4 : 6 : 7-*tetrachloroanthraquinone* (**II**), m.p. 259—260°, the constitution of which is established by its subsequent reactions. *m*-Hemipinic acid and *p*-$C_6H_4(OH)_2$ give 1 : 4 : 6 : 7-*tetrahydroxyanthraquinone* (**III**) (*tetra-acetate*, m.p. 192—193°). Gradual addition of a mixture of 4 : 5 : 1 : 2-$C_6H_2Br_2(CO)_2O$ and *p*-$C_6H_4(OH)_2$ to $AlCl_3$–NaCl at 200—220° yields 6 : 7-*dibromoquinizarin* (**IV**), m.p. 296—298°. (**III**) is reduced by Sn and HCl in AcOH to the 2 : 3-H_2-compound, converted by *p*-$C_6H_4Me{\cdot}NH_2$ and H_3BO_3 at 100° followed by atm. oxidation into 1 : 4-*di*-p-*toluidino*-6 : 7-*dihydroxyanthraquinone*. Similarly (**IV**) is transformed into its H_2-derivative, m.p. 287—289°, and thence into 6 : 7-*dibromo*-1 : 4-*di*-p-*toluidinoanthraquinone*. (**II**) and *p*-$C_6H_4Me{\cdot}NH_2$ at 165—175° slowly give 6 : 7-*dichloro*-1 : 4-*di*-p-*toluidinoanthraquinone*.

H. W.

Dyes related to toluidine-blue. C. F. H. Allen, C. V. Wilson, and G. F. Frame (*J. Org. Chem.*, 1942, **7**, 68—72).—4 : 8-*Di*-m-*toluidino*- (**I**), -p-*toluidino*-, -p-tert.-*amylanilino*- (**II**), -p-*anisidino*- (**III**), -p-*chloroanilino*- (**IV**), -p-*xenylamino*- (**V**), and -β-*naphthylamino*- (**VI**) -1 : 5-*dihydroxyanthraquinone* are obtained from 4 : 8-dichloroanthrarufin and the requisite base. Addition of H_3BO_3 is essential for the otherwise similar prep. of 4 : 8-*di*-o-*chloroanilino*-1 : 5-*dihydroxyanthraquinone*. The sulphonation of these compounds is described. The dyes from (**I**), (**III**), (**V**), and (**VI**) are much more sol. in H_2O than toluidine-blue (**VII**) and from the S : N ratio it appears that 2 SO_3H are present per N. The absorption curves of these dyes resemble that of the blue dye which results when (**VII**) is treated with fuming H_2SO_4 and has S : N > 1. (**II**) gives a dye resembling (**VII**) but apparently weaker. The dyes from (**V**) and (**VI**) absorb in the violet and are greenish, while that from (**IV**) does not have as high absorption in the far red. It appears that only *p*-alkylated amines can be expected to produce dyes closely resembling (**VII**).

H. W.

IV.—STEROLS AND STEROID SAPOGENINS.

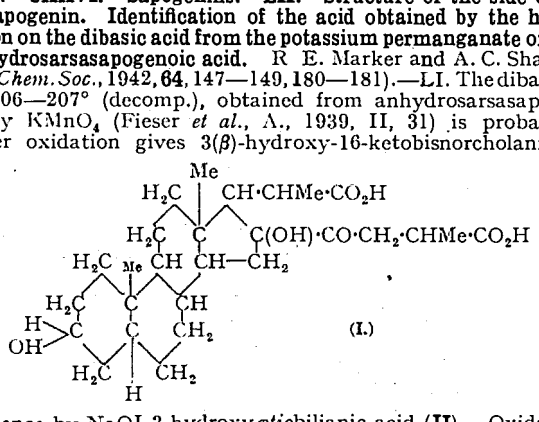
Preparation of $\Delta^{6:8(14)}$-, $\Delta^{7:9(11)}$-, $\Delta^{7:14}$-, and $\Delta^{8:14}$-cholestadienes. A., 1942, II, 167.

Relationship between optical rotatory power and constitution of sterols. II. S. Bernstein, E. J. Wilson, jun., and E. S. Wallis (*J. Org. Chem.*, 1942, **7**, 103—110).—Examination of $[\alpha]_D$ of a no. of sterols and the corresponding acetates, benzoates, and 3 : 5-dinitrobenzoates leads to the equation $[M]_{D\ \text{derivative}} = [M]_{D\ \text{sterol}} + \text{const.}$ The consts. for the acyl groups are quoted and depend on the group itself and on the mode of its union in the mol. Applications are discussed.

H. W.

Synthesis of an analogue of the sex hormones.—See A., 1942, II, 176.

Sterols. CXXV. Sapogenins. LI. Structure of the dibasic acid obtained by permanganate oxidation of anhydrosarsasapogenoic acid. Sterols. CXXVI. Sapogenins. LII. Structure of the side-chain of sarsasapogenin. Identification of the acid obtained by the haloform reaction on the dibasic acid from the potassium permanganate oxidation of anhydrosarsasapogenoic acid. R. E. Marker and A. C. Shabica (*J. Amer. Chem. Soc.*, 1942, **64**, 147—149, 180—181).—LI. The dibasic acid, m.p. 206—207° (decomp.), obtained from anhydrosarsasapogenoic acid by $KMnO_4$ (Fieser *et al.*, A., 1939, II, 31) is probably (**I**). Further oxidation gives 3(β)-hydroxy-16-ketobisnorcholanic acid,



(I.)

and thence by NaOI 3-hydroxy*ætio*bilianic acid (**II**). Oxidation of (**I**) by $KMnO_4$ at room temp. or of its Me ester acetate by CrO_3 and reduction of the product by Na–EtOH or –MeOH gives sarsasapogeninlactone.

LII. NaOI converts (**I**) into (**II**). (**I**) does not reduce $AgNO_3$–aq. NH_3 and is thus not an α-CO-acid (cf. *loc. cit.*).

R. S. C.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Absorption spectra of terpenoid compounds. II. Irone.—See A., 1942, I, 164.

Vapour-phase thermal isomerisation of α- and β-pinene. L. A. Goldblatt and S. Palkin (*J. Amer. Chem. Soc.*, 1941, **63**, 3517—3522).—Under optimum conditions, pure α-pinene, $[\alpha]_D$ +32·06°, is isomerised at 375° to α- [(CH·CO)$_2$O adduct, m.p. 91—92°] and β-pyronene [(CH·CO)$_2$O adduct, m.p. 163—164°] (α + β 12%), dipentene (~42%), and *allo*cimene (40%), b.p. 88·4°/20 mm. [(CH·CO)$_2$O adduct, m.p. 83—84°]. Pure β-pinene, $[\alpha]_D$ −21·81°, gives similarly myrcene (~67%), *l*-limonene (~13%), and α-camphorene (~9·5%).

R. S. C.

Reactions of β-pinene. I. With selenium dioxide in various solvents. W. D. Stallcup and J. E. Hawkins (*J. Amer. Chem. Soc.*, 1941, **63**, 3339—3341).—SeO_2 and β-pinene give pinocarvone, b.p. 75—78°/3 mm., 221—223°/760 mm., $[\alpha]_D^{20}$ −16·5° [semicarbazone, m.p. 212—213° (corr.); 2 : 4-*dinitrophenylhydrazone*, m.p. 223—223·5° (corr.)], and carvopinone (**I**), b.p. 82—84°/3 mm., $[\alpha]_D^{20}$ +62·7° (polymerises at 140° or when kept to a solid, softens at ~320°, and then melts with decomp.; semicarbazone, m.p. >300°; when distilled with $H_2C_2O_4$ in steam gives carvone and some polymeride). The amount of (**I**) formed depends partly on the solvent and, in general, increases with the time of reaction. The product of Dupont *et al.* (A., 1933, 1166) was a mixture.

R. S. C.

Diethylamides and some derivatives of camphor. M. Herold and E. Jirát (*Časopis Českoslov. Lék.*, 1938, **18**, 165—171).—Camphor-10-sulphonyl chloride, m.p. 67° (from the acid and PCl_5), with $NHEt_2$ gives the sulphondiethylamide, m.p. 50°. Camphoryl chloride (from the acid and PCl_5) similarly yields the di(diethylamide), m.p. 130°. Camphoric anhydride and $NHEt_2$ yield *NN*-diethyl-α-camphoramic acid, m.p. 166°. The pharmacological action of these diethylamides and that of camphor-3-carboxydiethylamide are studied in comparison with that of *o*-$C_6H_4(CO{\cdot}NEt_2)_2$. They show weak analeptic properties or little solubility in usable solvents.

F. R.

Camphorylidenesulphanilamides.—See B., 1942, III, 114.

American musk. I. Chemical constitution of the musk of the Louisiana muskrat. P. G. Stevens and J. L. E. Erickson (*J. Amer. Chem. Soc.*, 1942, **64**, 144—147).—The volatile oil (2·1%) from the scent glands of the Louisiana muskrat (*Ondatra zibethicus rivalicius*) contains dihydrocivetol (58), normuscol (40), and the derived odorous ketones (2%). The following data appear new. *cyclo*Heptadecane, m.p. 66·0—66·2° (lit. 65°). Dihydrocivet-oxime, m.p. 63—64°, and -2 : 4-*dinitrophenylhydrazone*, m.p. 84·5—86° after sintering. Normusc-2 : 4-dinitrophenylhydrazone, m.p. 108—109°, and -l-*menthylhydrazone*, m.p. 138·5—139·5°. Cryoscopic consts. of civetone and *cyclo*heptadecene are 39 and 20·2, respectively, the high val. of the former being probably due to intramol. conjugation of the CO and C:C.

R. S. C.

VI.—HETEROCYCLIC.

Tetrahydrofuran compounds. II. Preparation of γ-chloro-α-2-tetrahydrofurfurylbutane. R. D. Kleene (*J. Amer. Chem. Soc.*, 1941, **63**, 3539; cf. A., 1941, II, 266).—Furfurylideneacetone and H_2–NiO in EtOH at 125°/100 atm. (initial) give α-2-tetrahydrofurfuryl-*n*-butan-γ-ol (63%), a liquid, which with $SOCl_2$ at C_5H_5N at >50° gives γ-*chloro*-α-2-*tetrahydrofurfuryl*-n-*butane*, b.p. 58—60°/3 mm.

R. S. C.

Preparation of ω-furylpolyenealdehydes.—See A., 1942, II, 175.

Oxime of furfurylideneacetone. R. D. Kleene (*J. Amer. Chem. Soc.*, 1941, **63**, 3538).—*Furfurylideneacetoxime*, m.p. 88—90°, is prepared.

R. S. C.

Synthesis of 4-aminocoumarone-1 : 2-dicarboxylic acid *cyclo*hydrazide, a heterocyclic analogue of 4-aminophthalhydrazide. E. H. Huntress and W. M. Hearon (*J. Amer. Chem. Soc.*, 1942, **64**, 86—90).—Benzfuran-1 : 2-dicarboxylic acid and HNO_3 (1 conc. + 1 *d* 1·5) at 100° give the 4-NO_2-*acid* (**I**) (75%), m.p. 282—284°, which with $KMnO_4$–NaOH gives 2 : 5 : 1-OH·$C_6H_3(NO_2)$·CO_2H (proof of structure), but gives no anhydride. Its Me_2 ester (**II**) (CH_2N_2), m.p. 150—151°, gives no hydrazide, but evaporation of the acid with aq. N_2H_4 and heating the residue at 160—170° and then 195±5° gives 4-*nitrobenzfuran*-1 : 2-*dicarboxyl*cyclo*hydrazide* (**III**), m.p. 335—336° (*Ac*$_1$ derivative, m.p. 241—243°), also obtained by nitrating the unsaturated *cyclo*hydrazide. With $FeSO_4$–aq. NH_3, (**III**) gives 4-*aminobenzfuran*-1 : 2-*dicarboxyl*cyclo*hydrazide* (**IV**) (40%), decomp. ~330°. Hydrogenation (PtO_2) of (**II**) in AcOH gives Me_2 4-*aminobenzfuran*-1 : 2-*dicarboxylate*, m.p. 137—138°, and thence (**IV**). Hydrogenation of (**I**) gives the 4-NH_2-*acid*, m.p. >400°, which with CH_2N_2 gives Me_2 4-dimethylaminobenzfuran-1 : 2-dicarboxylate, m.p. 65—67°; the Ag salt is unchanged by MeI in xylene. Oxidation of (**IV**) gives less luminescence than does that of 4-aminophthalhydrazide.

R. S. C.

New reactions of 2-keto-1-benzylidenebenzfuran. I. T. B. Panse, R. C. Shah, and T. S. Wheeler (*J. Indian Chem. Soc.*, 1941, **18**, 453—456).—2-Keto-1-*p*-anisylidenebenzfuran (**I**) (reacts similarly to chalkones) and Br–$CHCl_3$ afford 1-*bromo*-2-*keto*-1-(*ω*-*bromo*-*p*-*methoxybenzyl*)*benzfuran*, m.p. 148°, converted by boiling MeOH or EtOH into 1-*bromo*-2-*keto*-1-(*ω* : *p*-*dimethoxy*-, m.p. 137°, or -(*p*-*methoxy*-*ω*-*ethoxy*-*benzyl*)*benzfuran*, m.p. 145°, respectively, or by 0·1N-KOH into 4′-methoxyflavonol. (**I**) and *cyclo*hexanonc in boiling EtOH–aq. NaOH yield 2-*keto*-1-[*ω*-(2′-*keto*-1′-cyclo*hexyl*)-*p*-*methoxybenzyl*]*benzfuran*, m.p. 278°, and (**I**) and CH_2PhBz (b.p.) or $CH_2Ac{\cdot}CO_2Et$–EtOH–NaOEt (reflux) afford 2-*keto*-1-(*β*-*benzoyl*-*β*-*phenyl*-*α*-*p*-*anisylethyl*)*benzfuran*, m.p. 243°, or *Et* 5-*p*-*anisylbenzfurano*-1′ : 2′ : 3 : 4-Δ²-cyclo*hexen*-1-*one*-6-*carboxylate* (**II**), m.p. 159° [*semicarbazone*, m.p. 253—255°; *oxime*, m.p. 183° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 209—210° (decomp.); *Cu* salt, m.p. 210°], respectively. (**II**) and 10% HCl at 160° give 5-*p*-*anisylbenzfurano*-1′ : 2′ : 3 : 4-Δ²-cyclo*hexen*-1-*one*, m.p. 152°.
A. T. P.

Isolation of a physiologically active tetrahydrocannabinol from *Cannabis sativa* resin. H. J. Wollner, J. R. Matchett, J. Levine, and S. Loewe (*J. Amer. Chem. Soc.*, 1942, **64**, 26—29).—The EtOH-extract (30%) of Indian charas is successively acetylated, fractionated at 0·001 mm., and subjected to chromatography. Fractionation at 0·015 mm. of a fraction, $[\alpha]_D^{21}$ −205° in EtOH, free from cannabidiol diacetate, and later chromatography gives a *tetrahydrocannabinol acetate* (**I**), $[\alpha]_D^{21}$ −214° in EtOH. (**I**) is unaffected by further fractionation or chromatography, has a potency 14·6 (±7·2%) relative to the 7 : 8 : 9 : 10-H_4-compound, is dehydrogenated by S at 225° or chloranil in xylene to cannabinol acetate, is hydrogenated to a H_6-compound, $[\alpha]_D^{21}$ −119° in EtOH, has absorption max. at 2745 (log ε 3·52) and 2805 A. (log ε 3·53), and with (*a*) acid–EtOH or NH_3–PhMe gives a *tetrahydrocannabinol*, (*a*) $[\alpha]_D^{21}$ −216° in EtOH, relative potency 8·04 (±22%), (*b*) absorption max. at 2760 (log ε 3·42) and 2820 A. (log ε 3·43), $[\alpha]_D^{22}$ ~−193° in EtOH.
R. S. C.

Osage orange pigments. VIII. Oxidation. M. L. Wolfrom and A. S. Gregory (*J. Amer. Chem. Soc.*, 1941, **63**, 3356—3358; cf. A., 1941, II, 267).—Pomiferin Me_3 or tetrahydropomiferin Me_3 or *iso*pomiferin Me_2 ether with H_2O_2 and a little KOH in aq. $COMe_2$ give 2 : 3-*epoxides* (yields: 80, 10, and 82%, respectively), m.p. 159·5°, 150—151°, and 200°, respectively (liberate I from hot, but not cold, KI–AcOH), yielding 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}CO_2H$ by more prolonged action in more conc. alkali. No epoxide was isolated from osajin, but *iso*osajin Me_2 ether gives a 2 : 3-*epoxide*, m.p. 199·5—200°, and thence *p*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$. These and known reactions prove that the *iso*flavone nucleus is not reduced in the H_4-derivatives and that neither the 2 : 3-ethylenic linking nor the OH of the 3-aryl nucleus is affected by the acid isomerisation, and fixes the positions of all but one OH.
R. S. C.

Anthochlor pigments of *Coreopsis gigantea*.—See A., 1942, III, 360.

Structure of glycollaldehyde dimeride. R. K. Summerbell and L. K. Rochen (*J. Amer. Chem. Soc.*, 1941, **63**, 3241—3244).—The dimeride (**I**) of $OH{\cdot}CH_2{\cdot}CHO$ is proved to be 2 : 5-dihydroxy-1 : 4-dioxan (cf. E. Fischer, A., 1895, i, 437). Dioxadiene and HBr–$CHCl_3$ at 0° give 2 : 5-dibromo-1 : 4-dioxan (**II**), darkens at 104—106°, decomp. 134°, converted by *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$,HCl (**III**) in 25% AcOH at 100° into $(\cdot CH{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2\text{-}p)_2$ (**IV**) and by AgOAc in PhMe at room temp. into 2 : 5-diacetoxy-1 : 4-dioxan (**V**), m.p. 157—158°. (**II**) and (**V**) are identical with the products obtained from (**I**) (H. O. L. Fischer *et al.*, A., 1927, 857). (*p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}CH{\cdot}CH_2)_2O$ could not be obtained by ozonolysis etc. of 2 : 5-dihydrofuran, only (**IV**) being isolated. Hydration of dioxene by boiling, very dil. HCl and then treatment with aq. (**III**) gives the p-*nitrophenylhydrazone*, m.p. 142°, of $OH{\cdot}[CH_2]_2{\cdot}O{\cdot}CH_2{\cdot}CHO$ (2 : 4-*dinitrophenylhydrazone*, m.p. 136°). This is converted into (**IV**) by boiling 25% AcOH [with or without addition of (**III**)] or boiling very dil. HCl, but is stable in boiling H_2O.
R. S. C.

2-Vinylthiophen. R. Kuhn and O. Dann (*Annalen*, 1941, **547**, 293—299).—2-Acetylthiophen and $Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$–N_2 at 108° give α-2-*thienylethyl alcohol* (**I**) (47%), b.p. 90·5°/11 mm. [5-HgCl derivative, m.p. 157° (block); *phenylurethane*, m.p. 85° (block)], with some 2-*thienylethyl* Pr^{β} *ether*, b.p. 75°/12 mm., 154° (decomp.)/755 mm. [hydrolysed by H_3PO_4; 5-HgCl derivative, m.p. 112—113° (block)], and *di*-α-2-*thienylethyl ether* (**II**), b.p. 121—122°/3 mm. [5 : 5′-(*HgCl*)$_3$ derivative, m.p. 196—198° (block)]; more prolonged reaction gives more of the ethers; in C_6H_6, (**I**) is accompanied by (**II**) and 2-*vinylthiophen* (**III**), b.p. 62—63°/50 mm. (**III**) is best obtained by boiling (**I**) with a little quinol; it can be titrated with *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ or $(CNS)_2$ but consumes 2 ICl; its colour reactions and absorption spectrum (max. 272 mμ.) are described; it polymerises when heated or kept, rapidly in O_2.
R. S. C.

9-Thiolphenanthrene and some of its derivatives. P. C. Dutta (*J. Indian Chem. Soc.*, 1941, **18**, 469—471).—K 9-phenanthrenesulphonate and PCl_5–$POCl_3$ at 140° give the chloride, converted by Zn–aq. H_2SO_4 at 100° (bath) into 9-*thiolphenanthrene* (**I**), m.p. 67°, and thence by I–EtOH into *diphenanthrenyl* 9 : 9′-*disulphide*, m.p. 149° (shrinks at 137°). (**I**) and AcCl (water-bath), or BzCl at 150—160°, or Me_2SO_4–aq. NaOH, yield 9-*acetyl*-, m.p. 93° (shrinks at 85°), 9-*benzoyl*-, m.p. 109° (shrinks at 95°), or 9-*methyl-thiolphenanthrene*, m.p. 75°, respectively. (**I**) and $(COCl)_2$ at room temp., followed by $AlCl_3$–CS_2 at room temp., then reflux, afford 4 : 5-*diketo*-4 : 5-*dihydrophenanthro*-9′ : 10′-2 : 3-*thiophen*, m.p. 245° (shrinks at 227°).
A. T. P.

5-Iodo-4 : 6-diketo-2-methyltetrahydropyridine-1-acetic acid.—See B., 1942, III, 114.

Isomeride of dimethylethylpyridine. R. H. Siddiqui (*J. Indian Chem. Soc.*, 1941, **18**, 505—506).—K_2 2 : 6-dimethyl-4-ethylpyridine-3 : 5-dicarboxylate (A., 1940, II, 53) is decarboxylated by short treatment with soda-lime, and after 4 months' contact the product gave no 2 : 6-dimethyl-4-ethylpyridine, but mainly an isomeride (+1·25H_2O), b.p. 195—196°, and a little of a base, b.p. 217—220°. The former base affords a *hydrochloride*, m.p. 197°, hydriodide, m.p. 155°, ethiodide, m.p. 185°, *platinichloride*, m.p. 222°, aurichloride, m.p. 180°, and *picrate*, m.p. 167° (anhyd. or +0·5H_2O).
A. T. P.

Structure of hydroxymethylene-methyl ethyl ketone and -methyl β-phenylethyl ketone. S. N. Joshi, R. Kaushal, and S. S. Deshapande (*J. Indian Chem. Soc.*, 1941, **18**, 479—484).—The $OH{\cdot}CH_2$ derivative (**I**) of COMeEt is $OH{\cdot}CH{:}CMe{\cdot}COMe$, whereas that of $Ph{\cdot}[CH_2]_2{\cdot}COMe$ is $Ph{\cdot}[CH_2]_2{\cdot}CO{\cdot}CH{:}CH{\cdot}OH$. (**I**) can be distilled without decomp. at 250 mm.; the titre of alkali against (**I**) in EtOH remains const. after 1 week, whereas that of (**II**) diminishes to nearly half of the val. (**I**) and $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ in EtOH–piperidine (water-bath) give 5-*cyano*-6-*hydroxy*-2 : 3-*dimethylpyridine*, m.p. 270°, converted by 50% H_2SO_4 at 150° into 6-*hydroxy*-2 : 3-*dimethylpyridine*-5-*carboxylic acid*, m.p. >280°, decarboxylated by distilling with a little Cu powder to 6-*hydroxy*-2 : 3-*dimethylpyridine*, m.p. 205° (distilled with Zn in H_2, it yields 2 : 3-dimethylpyridine). By similar reactions, (**II**) [*Cu* salt, m.p. 176° (decomp.)] affords 5-*cyano*-6-*hydroxy*-2-*β*-*phenylethylpyridine*, m.p. 198° (decomp.), and thence the -5-*carboxylic acid*, m.p. 211—212°, 6-*hydroxy*-2-*β*-*phenylethylpyridine*, m.p. 152°, and 2-*β*-phenylethylpyridine (platinichloride, m.p. 185°, blackens at 160°) [oxidised by aq. $KMnO_4$ to BzOH and picolinic acid (*Cu* salt, +2H_2O)].
A. T. P.

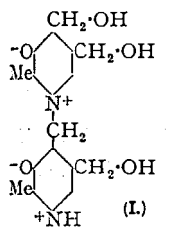
3 : 3-Di-(4′-hydroxy-2′-methyl-5′-*iso*propylphenyl)oxindole and some derivatives. E. Bureš and J. Kužel (*Časopis Českoslov. Lék.*, 1938, **18**, 199—208).—Condensation of thymol and isatin with $ZnCl_2$ at 120° yields the α-*isomeride* (**I**), m.p. 284° (decomp.), and condensation with conc. H_2SO_4, the *β*-*isomeride* (**II**), m.p. 284° (decomp.), of 3 : 3-*di*-(4′-*hydroxy*-2′-*methyl*-5′-iso*propylphenyl*)*oxindole*, differing probably according to whether attachment is made on the α- or *β*-CO of the isatin mol. (**I**) gives a Hg^{II} salt with $Hg(OAc)_2$ and Br_3-, m.p. 255° (decomp.), Ac_2, m.p. 168°, Ac_3, m.p. 144°, and Bz_2, m.p. 148°, derivatives. (**II**) gives a Hg^{II} salt with $Hg(OAc)_2$ and Br_3-, m.p. 248°, Cl_8-, m.p. 209°, Ac_2, m.p. 159°, Ac_3, m.p. 145°, and Bz_2, m.p. 147°, derivatives and 3 : 3-*di*-(4′-*methoxy*-2′-*methyl*-5′-iso*propylphenyl*)*oxindole*, m.p. 129°.
F. R.

2-Aminoacridine-7-sulphonamide. E. Aarons and A. Albert (*J.C.S.*, 1942, 183).—2-*Aminoacridine*-7-*sulphonamide*, m.p. 253° (decomp.), is prepared by reduction (Na–Hg–EtOH) of the 2-nitroacridone derivative. 2-Aminoacridine-7-sulphonic acid is similarly prepared using Al–Hg.
F. R. S.

***N*-Substituted derivatives of phenobarbital.** H. R. Henze and J. J. Spurlock (*J. Amer. Chem. Soc.*, 1941, **63**, 3360—3363).—Na phenobarbital (**I**) (dried at 140°) with boiling $Cl[CH_2]_2{\cdot}OH$ (excess; less well with 1 mol. in MeOH at 110°) gives 1-*β*-*hydroxyethylphenobarbital* (60%), m.p. 145—145·5° (not obtained from the Ag salt), converted by PCl_5 at 100° or PBr_3 at 110° into 1-*β*-*chloro*- (**II**) (stable to boiling H_2O), m.p. 112·5—113·5°, and 1-*β*-*bromo*-*ethylphenobarbital*, m.p. 127·5—128·5°. Phenobarbital, $OH{\cdot}CH(CH_2Br)_2$, and NaOMe–MeOH at 110° give *β*-*hydroxy*-*αγ*-*propylenedi*-1-*phenobarbital* (33%), a glass. With $COMe{\cdot}CH_2Br$ in boiling MeOH, (**I**) gives 1-*acetonyl*- (54%), m.p. 115—116° (2 : 4-*dinitrophenylhydrazone*, m.p. 223·5—224·5°), and 1 : 3-*diacetonyl*-*phenobarbital* (18%), m.p. 137·5—138° (stable to boiling H_2O; with N-alkali gives an acid, which at ~120° gives a gas). 1-*Phenacyl*- (49%), m.p. 159·5—160°, 1 : 3-diphenacyl- (37%), m.p. 156·5—157° (lit. an oil), 1-p-*bromophenacyl*- (32%), m.p. 149—149·5°, 1-p-*phenylphenacyl*- (44%), m.p. 195·5—196°, ? 1 : 3-di-*p*-phenylphenacyl-, an oil, -phenobarbital are similarly prepared. 1-*Propionyl*- (**III**) (43%), m.p. 96—96·5°, 1 : 3-*dipropionyl*- (**IV**), m.p. 108—109°, and 1-*α*-*bromo*-*α*-*ethyl*-*n*-*butyryl*- (**V**) (67%), m.p. 132—136°, -*phenobarbital* are obtained from Ag phenobarbital by $EtCOCl$–C_6H_6 or $CEt_2Br{\cdot}COBr$–PhMe, respectively. M.p. are corr. The products have little or no hypnotic effect, but some, notably (**II**)—(**V**), are anticonvulsants.
R. S. C.

Chemistry of vitamin-B_6. IV. Reactions in solutions at elevated temperatures. S. A. Harris (*J. Amer. Chem. Soc.*, 1941, **63**, 3363—3367; cf. A., 1942, II, 30).—Vitamin-B_6 in H_2O at 120° and p_H

6·5 (*i.e.*, conditions of sterilisation) gives the insol. *dimeride* (I) (6·4%), m.p. 205—209°, and later a gelatinous *polymeride*, $C_{24}H_{29}O_7N_3$. (I) is formed from the betaine form of *-B*$_6$ (A., 1941, II, 268); its structure is proved as follows. With MeI–C_5H_5N–MeOH it gives only a (mono)*methiodide hydriodide* (II), m.p. 197—198°, and with 48% HBr gives the $(CH_2Br)_3$ compound *dihydrobromide*, sublimes >230° (decomp.); *-B*$_6$ polymerises only in neutral solution, but its *N*-Me betaine and the 4-Me compound do not polymerise at all. The 4-Me ether at 120° gives a gelatinous polymeride with loss of OMe; in boiling CH_2Ph·OH, (I) gives the 4-*CH_2Ph ether* (III), m.p. 217—218°. In a borate buffer, (I) gives a faint dichloroquinonechloroimide test and a good colour in a veronal buffer, but (II) gives none. In boiling CH_2Ph·OH, *-B*$_6$ gives its 4-*CH_2Ph ether* (IV), m.p. 166·5° (*hydrochloride*, m.p. 144—145°), and (III). The structure of (IV) is shown by its positive $FeCl_3$ and dichloroquinonechloroimide test (borate buffer). In Bu^{a}OH, *-B*$_6$ gives the 4-*Bu^a ether hydrochloride* (V), m.p. 127—128° (cf. Scudi, A., 1941, III, 685). Relative curative doses are *-B*$_6$ 1, (I) 40, (IV) ~20, (V) <20. R. S. C.

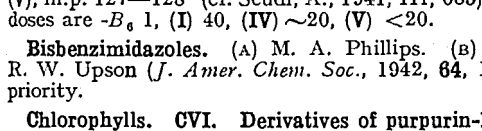


(I.)

Bisbenzimidazoles. (A) M. A. Phillips. (B) R. L. Shriner and R. W. Upson (*J. Amer. Chem. Soc.*, 1942, **64**, 187, 187—188).—Re priority. R. S. C.

Chlorophylls. CVI. Derivatives of purpurin-18. H. Fischer and H. Gibian. **CVII. Chloro-derivatives of chlorophyllporphyrins, phorbides, and chlorins.** H. Fischer and E. Dietl (*Annalen*, 1941, **547**, 216—233, 234—256; cf. A., 1942, II, 152).—Structures given below are supported by, and often deduced from, absorption spectra, which are detailed.

CVI. The absorption spectrum of the so-called oxime (I) (Zn salt) (Dietz *et al.*, A., 1934, 308) of purpurin-18 Me ester (II) (modified prep.) shows a shift towards blue; (I) thus probably contains the grouping (*A*) or (*B*). The same applies to the oxime Me ether (III).



(*A.*) (*B.*) (IV.)

The intermediate H hydroxylamide could not be isolated. Hydrolysis of (I) or (III) to chlorin-p_6 or a derivative thereof failed and the N·OMe of (III) is also unaffected. NaOMe or KOH–Pr^{a}OH gives only unstable, green metal salts. N_2H_4 and (II) similarly give an unstable, green H hydrazide, which yields the "*hydrazone*," sinters at 264°, $[\alpha]^{20}$ +930±200° in $COMe_2$ (white light) (Zn salt), analogous to (I) and also resistant to hydrolysis. Increase in basicity of the reagent permits isolation of the intermediate product. Thus NH_2Me and purpurin-18 in $COMe_2$ at room temp. give an acidic product, converted by esterification into *chlorin-*p_6*-carboxylmethylamide Me*$_2$ ester (IV), sinters at ~155° (Zn salt), which in conc. H_2SO_4 slowly, in alkali instantaneously, or with NaOH–C_5H_5N, NH_2OH, N_2H_4, or NH_2Me loses MeOH and gives the cyclic "*methylimide*" (V), m.p. >300° (Zn salt), analogous to (I). Piperidine and (II) at room temp. give a H piperidide (VI), converted by esterification into *chlorin-*p_6*-carboxylpiperidide Me*$_2$ ester (VII) [analogous to (IV)], m.p. 199° (*Zn* salt, sinters at ~280°, m.p. >300°), which cannot yield a cyclic product; (VI), obtained as above, is rapidly hydrolysed to (II) by dil. HCl, but if prepared by hydrolysis (NaOMe) or (VII), resists the action of acid. With NH_3–MeOH, (II) gives chlorin-p_6, but with semicarbazide gives a cyclic product analogous to (I). Mesopurpurin-18 [prep. by hydrogenation (Pd; dioxan) of the *Zn* salt, m.p. >300°, of (II)] gives analogously the cyclic *mesopurpurin-18 Me* ester "*oxime*," m.p. >260° (*Zn* salt; *Me ether*, sinters at ~245°, m.p. 260—280°), "*hydrazone*," m.p. >300° (Zn salt), and "methylimide" (Zn salt), and mesochlorin-p_6-carboxyl-methylimide and -piperidide Me$_2$ ester (Zn salts). The CHN_2·CO_2Et adduct of (II) reacts similarly giving products identical with the adducts from (I), (IV), and (V). HI–AcOH at 50° converts the cyclic products into those of the rhodopurpurin-γ-carboxylic anhydride series.

CVII. Phylloerythrin Me ester with H_2O_2 in 20% HCl at 10° and later CH_2N_2 gives 1-*chlorophylloerythrin Me* ester, sinters at 241°, m.p. >300° (purified by chromatography; impure Cu salt, m.p. 275°; *oxime*, m.p. >340°), and a small amount of the ? Cl_2-ester, sinters at 220°. Attempts to replace the Cl by CN led only to elimination of HCl, but the position of the Cl is proved by spectra and analogy. Phæoporphyrin-a_5 Me$_2$ ester gives similarly the 10-*Cl*-derivative, m.p. 272° (purified by chromatography; impure Cu salt, m.p. 205°). Mesomethylphæophorbide-*a* gives *chlorohydroxymesomethylphæophorbide*-a (VIII), m.p. 196°, $[\alpha]^{20}$ +438° in $COMe_2$ (white light) (oxime), converted by KOH–PrOH–Et_2O–C_5H_5N (little) at room temp. and then CH_2N_2 into *chlorohydroxymesopurpurin-7 Me*$_3$ ester, m.p. 176°, $[\alpha]^{20}$ +1700° in $COMe_2$ (white light) (also obtained from mesopurpurin-7 Me$_3$ ester); this gives the *Cu*, $[\alpha]^{20}$ +1250° in $COMe_2$ (white light), and *FeCl* derivative, m.p. 256°, $[\alpha]^{20}$ +4000° in $COMe_2$ (white light), of dihydroxymesopurpurin-7 Me$_3$ ester, which could not itself be obtained cryst. *Nitromesopurpurin-7 Me*$_3$ ester, m.p. 128°, is obtained by $NaNO_2$ in AcOH at 10°. Short treatment of (VIII) with hot KOH–MeOH–C_5H_5N and then CH_2N_2 gives dihydroxymesochlorin-e_6 Me$_3$ ester, m.p. 123°, cyclised by NaOH in boiling C_5H_5N. Mesorhodochlorin Me$_2$ ester gives a *product*, $C_{34}H_{38}O_5N_4Cl_2$, m.p. 150°, $[\alpha]^{20}$ +3250° in $COMe_2$ (white light), and later possibly a Cl_3-derivative. Purpurin-7 Me$_3$ ester gives a *product*, $C_{37}H_{38}O_7N_4Cl_2$, m.p. 151°. R. S. C.

Application of the *p*-hydrogen method to some problems of organic constitutions. I.—See A., 1942, I, 166.

Thiazoles. Synthesis of 2-phthalimidomethyl-4-diethylaminomethylthiazole. Y. F. Chi and S. Y. Tshin (*J. Amer. Chem. Soc.*, 1942, **64**, 90—91).—CH_2Cl·CN (prep. in 71% yield by heating the amide and P_2O_5 at 120—150° and then distilling at 200 mm.) and *o*-$C_6H_4(CO)_2NK$ at 120—130° give *phthalimidoacetonitrile* (77%), m.p. 118—120°, which with H_2S and a little $N([CH_2]_2$·$OH)_3$ in hot EtOH gives *phthalimidoacet-thioamide* (59%), sinters at 155°, m.p. 168—170°. With $CO(CH_2Cl)_2$ in hot abs. EtOH this gives 4-*chloromethyl-2-phthalimidomethylthiazole* (32%), m.p. 133—134·5°, converted by $NHEt_2$ in hot abs. EtOH into 2-*phthalimidomethyl-4-diethylaminomethylthiazole* (46%), m.p. 92—93°. R. S. C.

Thiazole sulphonamides.—See B., 1942, III, 115.

Azine dyes derived from 2 : 3-diketo-4 : 5 : 9′ : 10′-phenanthrathiophen. P. C. Dutta and R. M. Sinha (*J. Indian Chem. Soc.*, 1941, **18**, 477—478).—4 : 5-Diketo-4 : 5-dihydrophenanthra-9′ : 10′-2 : 3-thiophen and the respective *o*-diamine in AcOH yield 4 : 5 : 9′ : 10′-*phenanthrathiopheno*-2 : 3-*phenazine* [*phenanthra*-9″ : 10″-2′ : 3′-*thiopheno*-4′ : 5′ : 2 : 3-*quinoxaline*] (I), m.p. 255°, -2 : 3-2″-*chloro*-4″ : 5″-*tolazine*, m.p. 271° (shrinks at 265°), -2″ : 3″-*phenazine-azine*, m.p. 290°, and *-quinoxaline-azine*, m.p. 233—234°, respectively. A. T. P.

Thiazinocyanines. I. Carbocyanines containing the 2 : 4-benzthiazine nucleus. B. Beilenson and (Miss) F. M. Hamer (*J.C.S.*, 1942, 98—102).—3-Methyl-2 : 4-benzthiazine in C_5H_5N with 2-β-acetanilidovinylbenzoxazole ethiodide gives *trimethin*[2-(3-*ethyldihydrobenzoxazole*)][3-(2 : 4-*benzthiazine*)] (I), m.p. 138°, with the -6 : 7-benzbenzoxazole affords the -6 : 7-*benzbenzoxazole* derivative, m.p. 163°, and with the -benzthiazole (II) yields the *-benzthiazole* derivative (III), m.p. 199—200°; the -4 : 5-*benzthiazole*, m.p. 196°, and *-benzselenazole* derivatives, m.p. 212°, are similarly obtained. *p*-C_6H_4Me·SO_2Et and (I) followed by KI give [2-(3-*ethylbenzoxazole*)]-[3-(4-*ethyl*-2 : 4-*benzthiazine*)]*trimethincyanine iodide*, m.p. 237° (decomp.), and (III) similarly affords the *-benzthiazole* compound, m.p. 231—232° (decomp.). 3-Amino-2 : 4-benzthiazine and (II) yield γ-*azatrimethin*-[2-(3-*ethyldihydrobenzthiazole*)][3-(2 : 4-*benzthiazine*)], m.p. 145° (decomp.), and 3-*amino*-2 : 4-*benzthiazine ethiodide*, m.p. 220° (decomp.), and (II) afford [2-(3-*ethylbenzthiazole*)][3-(4-*ethyl*-2 : 4-*benzthiazine*)]-γ-*azatrimethincyanine iodide*, m.p. 240° (decomp.). Absorption max. of the various dyes have been compared. The effect of replacing the benzthiazole by the 2 : 4-benzthiazine nucleus in carbocyanine is to produce a hypochromic shift. F. R. S.

VII.—ALKALOIDS.

Azeotropism in the system nicotine–water. Separation of nicotine from related alkaloids by aqueous distillation. C. R. Smith (*Ind. Eng. Chem.*, 1942, **34**, 251—252).—An azeotropic mixture of nicotine (I) and H_2O (2·5 g. per 100 ml.) exhibits a b.p. lowering of 0·012°. (I) can be satisfactorily separated from nornicotine and anabasine by distilling with H_2O, making the distillate alkaline, and redistilling. C. R. H.

Alkaloids of *Rauwolfia canescens* (Linn.). II. (Miss) A. Mookerjee (*J. Indian Chem. Soc.*, 1941, **18**, 485—488; cf. A., 1941, II, 341). —"Rauwolscine" (I) [Me ester of (II)] and 10% aq. KOH at 100° (bath) give "rauwolscinic acid" (II), $[\alpha]_D^{23}$ +136·8° in H_2O [*hydrochloride*, m.p. 255·5—257·5° (decomp.) (+2·5H_2O or anhyd.); *picrate*, +EtOH, m.p. 232—234° (decomp.); *Et* ester, m.p. 234—236° (decomp.) {*hydrochloride*, m.p. 262—264° (decomp.); *picrate*, m.p. 179·5—181·5° (decomp.)}; *Pr^a* ester, m.p. 206—208° (decomp.) {*hydrochloride*, m.p. 264—266° (decomp.)}; *Bu^a* ester, m.p. 181—182·5° (decomp.), after frothing at 105—106° {*hydrochloride*, m.p. 251—253° (decomp.)}]. Absorption curves of the hydrochlorides of yohimbine and (I) are very similar. A. T. P.

Isolation of a new alkaloid from perennial ryegrass. J. Melville and R. E. R. Grimmett (*Nature*, 1941, **148**, 782).—*Perloline* (I), $C_{36}H_{22}O_3N_4(OMe)_4$, has been isolated from *Lolium perenne*, L. (I) is sol. in EtOH and $CHCl_3$, slightly sol. in $COMe_2$, Et_2O, and H_2O. Dil. solutions in $CHCl_3$ are golden-yellow with a green fluorescence that can be detected in ordinary light at a concn. of 1 in 5×10^6. (I) is reduced by $TiCl_3$ to a colourless material, which can be oxidised quantitatively by $Fe(CN)_6'''$. The grass may contain from 3 μg. to 1 mg. per g. dry wt. Other alkaloids have been found in ryegrass. L. S. T.

Alkaloid nicotinates.—See B., 1942, III, 86.

VIII.—ORGANO-METALLIC COMPOUNDS.

Metallation of triphenylarsine. H. Gilman and C. G. Stuckwisch (*J. Amer. Chem. Soc.*, 1941, **63**, 3532—3533).—$AsPh_3$ and $LiBu^a$ in Et_2O give the 3-Li derivative (**I**), which with CO_2 gives a gummy acid, converted by $KMnO_4$ into *diphenyl-m-carboxyphenylarsine oxide* (**II**), m.p. 215°. *m*-$C_6H_4Me{\cdot}MgBr$ and $AsPh_2Cl$ in Et_2O give *diphenyl-m-tolylarsine* (72%), m.p. 170—173° [$HgCl_2$ derivative, m.p. 201—202°; also obtained (2·7%) from (**I**) by Me_2SO_4], slowly oxidised to (**II**) by aq. $KMnO_4$ at 60°. R. S. C.

Relative reactivities of organo-metallic compounds. XLIII. Introduction of aminoaryl groups by the halogen–metal interconversion reaction. H. Gilman and C. G. Stuckwisch (*J. Amer. Chem. Soc.*, 1941, **63**, 2844—2855; cf. A., 1942, II, 41).—*p*-$C_6H_4Br{\cdot}NH_2$ and $LiBu^a$ in Et_2O at −60° give [max. (≯68%) in 9 min.] *p*-$Li{\cdot}C_6H_4{\cdot}NH_2$ (**I**), as judged by the yield of acid obtained. With $AsPhCl_2$ in Et_2O at, successively, −45°, room temp., and the b.p., (**I**) gives 63% (over-all) of *As Ph di-p-aminophenyl* [4 : 4′-*diaminotriphenylarsine*], m.p. 69°, which with *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$–$C_5H_5N$ and later hydrolysis by aq. NaOH gives *As Ph di-p-sulphanilamidophenyl* (**I**), m.p. 198° ($N^4N^{4\prime}$-Ac_2 derivative, m.p. 184°). $PPhCl_2$ similarly gives 64% of *P Ph di-p-aminophenyl*, an oil (Ac_2 derivative, m.p. 169°), and *di-p-sulphanilamidophenyl*, m.p. 202—204° [does not depress the m.p. of (**I**); Ac_2 derivative, m.p. 186—187°]. R. S. C.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Hydrolytic derivatives of lignin volatile compounds. A. Bailey (*J. Amer. Chem. Soc.*, 1942, **64**, 22—23).—The volatile products (27·5%) obtained from BuOH-lignin of Western hemlock by HCl–BuOH–H_2O at 160° contain $COMe_2$ 1·9, Pr^aCHO 1·6, MeOH 2·5, $CH_2{:}CH{\cdot}CH_2{\cdot}OH$ 2·5, Pr^aOH 4·8, HCO_2H (as Bu ester) 11·4, and $CHEt{:}CMe{\cdot}CHO$ 2·8%. A non-volatile C_6H_6-sol. and a resinous alkali-sol. fraction were also formed. R. S. C.

Mechanism of chlorination of lignin. E. V. White, J. N. Swartz, Q. P. Peniston, H. Schwartz, J. L. McCarthy, and H. Hibbert (*Paper Trade J.*, 1941, **113**, *TAPPI Sect.*, 299—309).—The reactions involved in the chlorination of lignin (**I**) and of unbleached wood pulp by aq. Cl_2 are discussed. With isolated alkali-(**I**), treatment with aq. Cl_2 results in almost equiv. chlorination and demethoxylation to a degree which increases with increase in the % of Cl added and also with the acidity of the reaction mixture. It is believed that chlorination takes place at either the 6- or the 5-positions of the guaiacyl nuclei of (**I**), depending on whether the *p*-OH groups of these nuclei are free or not. Furthermore, the presence of such Cl atoms induces instability in the OMe groups, which then split off with the formation of quinone or diketo-structures which may then undergo further fission to yield acidic groups in the (**I**). The rate of Cl_2 consumption by ligninsulphonic acid can be accounted for by assuming that the process involves two main reactions, the initial one rapid, and the second slow (second order). The former is one of chlorination and demethoxylation as evidenced by the correlation found to exist between the rate of Cl_2 consumption and the rate of introduction of Cl and accompanying loss of OMe by the (**I**). The latter appears to be essentially an oxidation process in view of its similarity to the second-order internal oxidation reaction involved in the self-decomp. of aq. Cl_2. During aq. acidic chlorination of unbleached pulp little (**I**) is removed, but it is made potentially sol. in alkali, presumably as a result of the formation of CO_2H groups at points from which OMe was split. The removal of chlorinated (**I**) from pulp is shown to be largely a physical process in which such factors as temp. and time of treatment control the degree of dissolution of the (**I**) by the alkaline medium. H. A. H.

XI.—ANALYSIS.

Improved distilling column head.—See A., 1942, **I**, 188.

Immersion still-head for low-pressure distillation of organic mixtures.—See A., 1942, I, 188.

Chromatography of solutions containing a single solute.—See A., 1942, I, 159.

Modifications in the Dumas micro-method for nitrogen. Automatic apparatus for combustion micro-methods. G. L. Royer, A. R. Norton, and F. J. Foster (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 79—82).—Combustion furnaces, auxiliary control equipment, and procedure are described. Tank CO_2 is used, and gives a const. blank of 0·010 c.c. per determination. The automatic combustion method gives results that are as accurate as, and more reproducible and quicker than, those given the standard Pregl procedure. A single determination requires 40 min. L. S. T.

Aliphatic sulphinic acids. I. Analysis and identification.—See A., 1942, II, 162.

Identification of alcohols in aqueous solution.—See A., 1942, II, 161.

Electrophotometric microdetermination of phosphorus in lipin extracts.—See A., 1942, III, 428.

Gasometric determination of carboxyl groups in free amino-acids. Determination of free amino-acids by titration of carbon dioxide formed in reaction with ninhydrin. D. D. Van Slyke, D. A. MacFadyen, and P. Hamilton (*J. Biol. Chem.*, 1941, **141**, 627—669, 671—680; cf. A., 1938, II, 211).—α-NH_2-acids boiled in H_2O with an excess of ninhydrin (**I**) (chloramine-*T* is less satisfactory) at p_H 1—5 evolve the CO_2 of their CO_2H groups quantitatively in a few min.; details and apparatus are described. Proline and hydroxyproline yield their carboxylic CO_2 similarly. Structures which react are $NH_2{\cdot}CHR{\cdot}CO_2H$ and $CH_2R'{\cdot}NH{\cdot}CHR{\cdot}CO_2H$. When NH_2 is in β or γ position, reactivity of the CO_2H is diminished. Under the conditions used the following give no CO_2: peptides, except where $\cdot C(NH_2){\cdot}CO_2H$ is present, *e.g.*, glutathione; acetylated and benzoylated NH_2-acids; derivatives with no H on NH_2-N; acid esters (*e.g.*, glycine ester) or amides; simple org. acids, *e.g.*, AcOH; OH-acids, *e.g.*, lactic, citric; keto-acids, *e.g.*, $AcCO_2H$. Glutamic acid evolves CO_2 from 1 CO_2H only; creatinine and (**I**) in H_2O react only slightly at p_H 2·5, but CO_2 is evolved in boiling AcOH. The property of aspartic acid (like cystine) to evolve 2 mols. of CO_2 with (**I**) permits its determination in mixtures containing most of the other NH_2-acids (not lysine or proline) yielded by protein hydrolysis. In digestion of casein to peptides by cryst. trypsin no free NH_2-acid is liberated (cf. 20% liberation with crude trypsin). CO_2 is determined by distilling in vac. into $Ba(OH)_2$, and excess of the latter is titrated. A. T. P.

Determination of pentoses with hydrobromic acid. G. Jayme and P. Sarten (*Naturwiss.*, 1940, 28, 822—823).—The sample is distilled with 20—30% HBr to obtain 400—800 c.c. of distillate, H_2O being added to the distilling flask as is necessary. Furfuraldehyde is determined in the distillate with barbituric or thiobarbituric acid, and a correction applied for the solubility of the ppt. J. L. D.

Colorimetric determination of phenothiazine. H. L. Cupples (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 53).—The phenothiazine in EtOH is treated with an excess of aq. Br kept at 60°, the excess of Br boiled off, the solution filtered, and the red colour determined photometrically. The accuracy is ±6%. J. D. R.

Colour reactions of reducing pyrimidines. E. B. Knott (*J.S.C.I.*, 1941, **60**, 313—314).—Aq. solutions of reducing pyrimidines give characteristic colour changes when treated with 0·1N-KI–I, then 1 drop of aq. NH_3 (dil.) followed by EtOH and HCl. A table is given showing how the compounds fall into four groups according to the no. and position of the NH_2-groups in the 4-, 5-, or 6-positions. The test can be adapted for micro-identification. W. C. J. R.

Iodosulphate microchemical identification tests for cinchona alkaloids. C. C. Fulton (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 848—850).—Three reagents are described, all consisting of varying proportions of I–KI in aq. AcOH–H_2SO_4. These reagents give with quinine, quinidine, cinchonine, and cinchonidine characteristic cryst. ppts., readily identified under the microscope. Numerous photomicrographs are reproduced. J. D. R.

Reactivity of porphyrindin in presence of denatured proteins. J. P. Greenstein and W. V. Jenrette (*J. Biol. Chem.*, 1942, **142**, 175—180).—The advantages and disadvantages of the method of determination of SH groups in native and denatured proteins by titration with porphyrindin (**I**) are discussed. The method has been improved by the use of Na nitroprusside as an outside indicator, by standardising the (**I**) solutions against cysteine during the course of the titration with protein, and by modifying the method so as to provide a stepwise and rapid determination of the protein SH groups. When cysteine is added in varying amounts to denatured proteins, it is nearly quantitatively recovered by subsequent titration of the mixtures with (**I**), and there is little, if any, interference by other reducing groups of the proteins, as these react too slowly under the conditions of the method. Data on the SH group content of denatured tobacco mosaic virus protein and of ovalbumin, obtained by the use of various oxidants and sol. denaturing agents, which show good agreement, are compared and discussed. J. N. A.

Determination of hydroxylysine in proteins. D. D. Van Slyke, A. Hiller, and D. A. MacFadyen (*J. Biol. Chem.*, 1941, **141**, 681—705).—Hydroxylysine (**I**) is pptd. from protein hydrolysates with other diamino-acids by phosphotungstic acid, and is determined by the NH_3 liberated from the group $\cdot CH(OH){\cdot}CH(NH_2)\cdot$ with $NaIO_4$. Other NH_2-acids, *e.g.*, serine, threonine, also give quant. yields of NH_3, and these are separated from (**I**) by crystallising the phosphotungstates. In only gelatin and collagen of the proteins analysed did the amount of (**I**) approach 1% of the total protein-N. A. T. P.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JUNE, 1942.

I.—ALIPHATIC.

Mechanism and chemical kinetics of organic reactions in liquid systems. E. D. Hughes (*Nature*, 1942, **149**, 126—130).—A summarised discussion. A. A. E.

Production of Δ^{β}-olefines.—See B., 1942, II, 90.

Synthesis of *iso*olefinic and paraffinic hydrocarbons containing a quaternary carbon atom. I. Reaction between the hydrobromides of isoprene and $\alpha\alpha\gamma$-trimethylbutadiene and magnesium *cyclo*hexyl chloride. R. J. Levina, A. M. Paniuschkina, N. A. Schtscheglova, N. A. Smirnova, K. D. Schtscherbakova, and N. I. Schor (*J. Gen. Chem. Russ.*, 1941, **11**, 411—422).—The interaction between Mg *cyclo*hexyl chloride (**I**) and the two isomeric hydrobromides of isoprene [$\alpha\alpha$- and $\gamma\gamma$-dimethylallyl bromide] leads to the formation of a mixture of $\alpha\alpha$-dimethylallyl*cyclo*hexane, possibly contaminated with di*iso*amyl, and of $\gamma\gamma$-*dimethylallyl*cyclo*hexane*, b.p. 101—102·5°/40 mm. $\alpha\alpha\gamma$-Trimethyl-$\Delta^{\alpha\gamma}$-butadiene (**II**) is prepared from CMe_2:CH·COMe and MgMeI. Rapid decomp. of the resulting mixture by dil. AcOH leads to the monomeric form of (**II**), whereas slow decomp. gave a dimeric form. A H_4-derivative of the dimeride has b.p. 95—96°/11 mm. With HBr (**II**) gives the unstable $\alpha\alpha\gamma\gamma$-tetramethylallyl bromide, b.p. 71—72°/80 mm., which with (**I**) gives δ-cyclo*hexyl-ββδ-dimethyl-*Δ^{β}*-pentene*, b.p. 101—102°/16 mm., identified by oxidation with $KMnO_4$ to dimethyl*cyclo*hexylacctic acid. N. G.

Preparation of $\alpha\alpha\alpha$-trifluoro-β-chloroethane.—See B., 1942, II, 90.

So-called "vitamin-A_2." P. Karrer, A. Geiger, and E. Bretscher (*Helv. Chim. Acta*, 1941, **24**, 161—172E).—The unsaponifiable matter of the liver oils of fresh-water fish has been chromatographed over $Ca(OH)_2$, which removes the bulk of the sterols and similar compounds and, in particular, a red oil, and fibrous clay, which achieves a partial separation of vitamin-A_2 from -A, the former being the more readily adsorbed. Complete separation cannot be effected and neither substance is completely unaltered by the operation. The ratio -A_2 : -A in the product is ~3·5 : 1. The observation that the absorption band of -A_2 is displaced by only ~15—17 mμ. from that of -A and that the b.p. of the compounds are very similar suggests that -A_2 is CMe_2:CH·$[CH_2]_2$·[CMe:CH·CH:CH]$_2$·CMe:CH·CH_2·OH and thus stands in the same relationship to -A as does lycopene to β-carotene. When degraded with O_3 -A_2 gives ~50—70% of the theoretically possible amount of $COMe_2$ but no CO_2H·CMe_2·CH_2·CO_2H. -A_2 does not appear to be a vitamin for mammals since the action of -A–A_2 mixtures of known -A content can be explained by the -A present. In quest of a synthesis of -A_2, crude β-ionylideneacetaldehyde is condensed with β-methylcrotonaldehyde in presence of $NaNH_2$ but no product results which gives a blue or green colour with $SbCl_3$. With piperidine acetate as condensing agent a material is formed which gives a green colour with $SbCl_3$–$CHCl_3$; this becomes blue after reduction with $Al(OPr^{\beta})_3$. Chromatographic separation shows the product to be non-homogeneous and there is no fraction giving the bands typical of -A_2 in the Carr–Price reaction. H. W.

Denatured alcohol containing mesityl oxide.—See B., 1942, II, 91.

Manufacture of olefine chlorohydrins.—See B., 1942, II, 91.

Production of glycols.—See B., 1942, II, 91.

Determination of diethylene glycol monoethyl ether.—See B., 1942, II, 89.

Action of alkaline hydrogen peroxide on phosphoric esters. Glycerophosphate-mutase. J. Courtois and P. Biget (*Compt. rend.*, 1941, **213**, 192—193).—At room temp., alkaline (NaOH, NH_3) H_2O_2 decomposes phosphoric esters which contain free :CO or ·CHO but not others (*e.g.*, Me, Pr, α- and β-glyceryl). Glycollaldehyde (1 mol.) with 2 H_2O_2 yields HCO_2H (2 mols.), H_3PO_4, and H_2O and hexose diphosphate (1 mol.) with 5 H_2O_2 yields (chiefly) HCO_2H (4 mol.), phosphoglycollic acid (1 mol.), and 4 H_2O. α- (**I**) is determined in complex biological media containing β-glycerophosphate (**II**) by enzymic (mutase) conversion of (**II**) into (**I**), removal of inorg. PO_4''' with $Ba(OAc)_2$ at p_H 8·5, oxidation with HIO_4 of (**I**) to phosphoglycollaldehyde, decomp. of this with alkaline H_2O_2, and determination of the H_3PO_4 produced. The enzyme is not found in barley, the seeds of almond, peach, or poppy, spinach leaves, autolysed pig kidney, extract of placenta, urine, or human blood serum or erythrocytes. Under ordinary conditions it does not dephosphorylate (**II**). W. McC.

Production of thiols.—See B., 1942, II, 91.

Production of carboxylic acids.—See B., 1942, II, 92.

Determination of volatile fatty acids.—See A., 1942, II, 211.

Manufacture of lower aliphatic acid anhydrides.—See B., 1942, II, 92.

Electrolysis of diethylacetic acid in mixture with its alkali metal salts and with addition of nitrates.—See A., 1942, I, 208.

Highly unsaturated ester from *Matricaria inodora*, L. N. A. Sörensen and J. Stene (*Annalen*, 1941, **549**, 80—94).—Distillation of the flowers in steam gives a "Matricaria-*ester*" (**I**) (0·1—0·2%), $C_{11}H_{10}O_2$, m.p. 37°, the odour of which differs from that of the flowers. (**I**) has mol. exaltation 8·27, is very unstable in air (stable at <−10°/vac.), absorbs 6 H_2 (Pt–SiO_2 gel; EtOH) to give *n*-C_9H_{19}·CO_2Me (**II**) (hydrolysed to the acid for identification), with KOH–EtOH at 0° gives an *Et* ester, $C_{12}H_{12}O_2$, m.p. 19·5°, and is hydrolysed by very dil. NaOH at 0° to the *acid*, $C_{10}H_8O_2$, sinters at 96°, m.p. 98—99° [reconverted into (**I**) by CH_2N_2–Et_2O]. When boiled in 5N-NaOH and then distilled in steam, (**I**) gives CH_2:CH·COMe [identified as *p*-nitrophenylhydrazone (Debye spectrum)], probably by way of CHAc:CH·CO_2H. These properties and analogy with CPr^{α}:C·C:C·CH:CH·CO_2Me (**III**) (Viljams *et al.*, A., 1936, 259) suggest that (**I**) is *Me* n-*deca*-$\Delta^{\alpha\eta}$-*diene*-$\Delta^{\gamma\varepsilon}$-*di*-*inenoate*. Isolation of malcic acid from (**III**) (*loc. cit.*) proves the *cis*-nature of the Δ^{α}-C:C. Ultra-violet illumination of (**I**) in light petroleum–N_2 gives an isomeric "trans"-*ester* (**IV**), m.p. −2° to −1°, b.p. 79·5—80° (bath)/0·01 mm., hydrogenated to (**II**) and hydrolysed to a trans-*acid*, sinters at ~50° (? isomerisation), resolidifies, m.p. 83—87°, reconverted into (**IV**) by CH_2N_2. With Zn dust in Ac_2O–C_5H_5N, (**I**) gives an unstable H_2-ester, b.p. 85°/0·01 mm., having an odour of *M. discoidea*, DC, and possibly being CHEt:C:C:C:C:CH·CH_2·CO_2Me. Biogenesis of (**I**) and (**III**) probably follows a terpene-like route, starting from AcCHO and $AcCO_2H$ (cf. *loc. cit.*). R. S. C.

Reaction of non-conjugated unsaturated fatty acid esters with maleic anhydride. W. G. Bickford, P. Krauczunas, and D. H. Wheeler (*Oil and Soap*, 1942, **19**, 23—27).—When heated in evacuated sealed tubes at 200° or 250° with excess of (:CH·CO)$_2$O (**I**), Me oleate (**II**), linoleate (**III**), and linolenate (**IV**) react with 1, 2, and 2·5 mols. of (**I**) respectively; the I vals. of the products, however, show that the unsaturation of (**II**) is unaffected by the reaction. In the case of (**III**) the first mol. of (**I**) reacts chiefly to saturate one double linking, whilst the second adds without further affecting the degree of unsaturation; in the case of (**IV**) addition of the first two mols. only of (**I**) causes corresponding reduction in unsaturation. It is suggested that the mechanism of the addition of (**I**) causing saturation comprises a shifting of the double linkings of the polyethenoid esters to a conjugated configuration followed by a Diels–Alder addition of (**I**). In the case of (**II**) and the final reaction of (**III**) and (**IV**) a mol. of (**I**) may add at one of the C atoms in the remaining double linking, or at an adjacent one, to form a substituted succinic anhydride without affecting the unsaturation of the ester. E. L.

Chemistry of the fatty acids. IX. Spectroscopic study of methyl arachidonate purified by crystallisation and distillation and its alkali isomerisation product. X. Structure of arachidonic acid as evidenced by oxidative degradation and selective hydrogenation. D. T. Mowry, W. R. Brode, and J. B. Brown (*J. Biol. Chem.*, 1942, **142**, 671—678, 679—691).—IX. Examination of the relationship between n_D^{20} and I val. of fractions obtained by the distillation of Me arachidonate (**I**) indicates the presence of ~5% of Me oleate and of a viscous, yellow material of higher b.p. which appears to be mainly an oxidised (and possibly isomerised) form of (**I**). The absorption spectra of the samples show even better than the diene val. and mol. refraction that they are relatively free from conjugated unsaturation. The kinetics of the isomerisation by alkali of arachidonic acid (**II**) have been followed spectroscopically and the similarity to the behaviour of the $\Delta^{\alpha\delta\eta}$-triene system present in linolenic acid is noted. The isomerised acid, m.p. 95—98°, is rapidly

oxidised and polymerised on exposure to light and air, becoming sticky and yellowish.

X. Ozonolysis of (I) gives hexoic (III), acetic, glutaric (IV), succinic (V), and malonic acid, MeCHO, and CO_2, whilst oxidation with $KMnO_4$ in $COMe_2$ affords (III), (IV), (V), and $H_2C_2O_4$. (II) is therefore $\Delta^{\delta\eta\kappa\nu}$-eicosatetraenoic acid. Hydrogenation of (I) proceeds in two stages, the diethylenic intermediate product consisting of 80—90% of Me Δ^{ν}-eicosadienoate and 5—10% of Me Δ^{η}-eicosadienoate. H. W.

Peroxides derived from η-aldehydo-octoic acid and nonaldehyde. Bis-α-hydroxy-ω-earboxyoctyl peroxide and bis-α-hydroxynonyl peroxide. G. King (*J.C.S.*, 1942, 218—220).—η-Aldehydo-octoic acid and nonaldehyde with H_2O_2–AcOH afford bis-α-hydroxy-ω-carboxyoctyl peroxide, m.p. 112·5° (lit. ~98°), and bis-α-hydroxynonyl peroxide, m.p. 78° (lit. 72°), respectively. The latter is an unstable solid and both dissociate in solution; a study of the peroxidising properties has been made. W. C. J. R.

Derivatives from hydrogenated castor oil. I. λ-Hydroxystearic acid and its alkyl esters. S. A. Bell and A. Taub (*J. Amer. Pharm. Assoc.*, 1942, **31**, 75—81).—The acid, m.p. 81°, isolated from hydrogenated castor oil yielded the following esters: *Me*, m.p. 56·5—57·0°, *Et*, m.p. 50·3—51·6°, *Pr*$^{\alpha}$, m.p. 48·3—49·5°, *Bu*$^{\alpha}$, m.p. 43·7—44·9°, n-*amyl*, m.p. 45·0—46·0°, n-*hexyl*, m.p. 46·1—47·4°, n-*octyl*, m.p. 49·5—51·3°, n-*decyl*, m.p. 56—57·2°, *lauryl*, m.p. 60—61·5°, myristyl, m.p. 61—64°, *cetyl*, m.p. 66·5—69·5°, and *stearyl* λ-*hydroxystearate*, m.p. 76·0—76·5°. Data for solubilities of the esters and for characteristics of their mixtures are tabulated. The possible application of the esters to ointments and similar bases is discussed. F. O. H.

Oxidation of hydroxyketostearic acid in presence of alcoholic alkali. T. P. Hilditch and H. Plimmer (*J.C.S.*, 1942, 204—206).—The oxidation of a mixture of isomeric θι-dihydroxyketostearic acids in alkaline solution is shown to depend on the excess of KOH. At 20° the yields of azelaic (I), nonoic (II), and dihydroxystearic acids (III) increase with [KOH]. Similarly at 50° the yields of (I) and (II) increase but that of (III), which is 41% with an excess of 1 mol. of KOH, decreases. The reaction is completed in 8 hr. and it is not necessary to pass fresh O_2 through the mixture. It is suggested that the reaction proceeds ·CH(OH)·CO· → ·CO·CO· + ·CH(OH)·CH(OH)· → (I) and (II). W. C. J. R.

Preparation of substituted malonic acid derivatives.—See B., 1942, II, 93.

Purification of maleic anhydride.—See B., 1942, II, 93.

Complexes of dehydroascorbic acid with three sulphydryl compounds. B. B. Drake, C. V. Smythe, and C. G. King (*J. Biol. Chem.*, 1942, **143**, 89—98).—Dehydroascorbic acid is mixed with glutathione, $SH{\cdot}CH_2{\cdot}CO_2H$, or cysteine, in aq. AcOH, and in each case, changes in optical activity and in the amount of I required for titration of the mixtures, and also calculation of equilibrium consts., indicate that equimol. amounts of the two components of each mixture react to form a complex. A. T. P.

Pectin substances. Isolation, properties, and constitution of flax pectin and its cleavage products. M. Lüdtke and H. Felser (*Annalen*, 1941, **549**, 1—43).—Flax dust is washed successively with CH_2Cl_2, cold very dil. HCl, and H_2O, and then extracted with 0·5% aq. $(NH_4)_2C_2O_4$ at 45° or 80°; the aq. solution is conc. and then poured into EtOH or MeOH containing a little HCl. Several repetitions of this pptn., followed by dialysis, give a pectin (I) of const. properties: orcinol and naphthoresorcinol reactions positive, p_H 3·38 (glass electrode), 3·16 (quinhydrone), $[\alpha]_D^{20}$ +250—260° in 0·1N-NaOH, acid val. ~400 before hydrolysis or ~510—520 after hydrolysis by 0·1N-NaOH or aq. $Ca(OH)_2$, 2·3% of esterified MeOH, 0—0·5% of ash, and traces of $NH_4^{\cdot}$. It gels readily in H_2O but is sometimes too insol. to give a 1% solution. Omission of the HCl-wash lowers the yield. $(NH_4)_2C_2O_4$ may be replaced by NH_4 citrate or lactate, $Na_2C_2O_4$, $NaHCO_3$, NH_4HCO_3, or very dil. NaOH (until neutral), but the alkaline salts cause some hydrolysis of CO_2Me; extraction by H_2O or aq. sucrose gives poor yields. Yields are much best (12—14%) from unretted green flax dust (cells attached to the fibre walls and obtained as dust during technical treatment of the fibre); the whole unretted fibre gives 3—4%, other parts less. Retting reduces the yield greatly owing to microbiological decomp. (see below). (I) differs from other previously described flax pectins, which were all more or less degraded. (I) is sol. in aq. NH_3 or very dil. aq. NaOH or NH_3–CuO. Conc. NH_3–CuO ppts. an insol. pale blue product, which after purification has $[\alpha]_D^{20}$ +254—265°, acid val. 425—502, yields a little ash, and does not swell. Conc. alkali ppts. an alkali-pectin (II) $[\alpha]_D^{20}$ +250—276·5°, acid val. 418—510, ash 0·5—2·19%, from which all the esterified MeOH has been removed; (II) swells but gives an inhomogeneous solution of lowered η. Various methods of determining OMe in (I) give 2·3—4%; the higher vals. are due to anhydride linkings; the OMe thus exists entirely as CO_2Me; the low OMe content refutes the generalisation (lit.) connecting this val. with ability to gel. With 0·2—0·5% HCl or H_2SO_4 at 100°, (I) gives ~3% of arabinose (III) (determined as 2 : 4-dinitrophenylhydrazone) and an acid-pectin (IV), $[\alpha]_D^{20}$ +280—288°, acid val. 498 before hydrolysis, 562 after hydrolysis, which retains the OMe, does not swell, and is insol. Dil. lactic acid causes a similar change more slowly. (IV) is a polygalacturonic acid, partly esterified with MeOH and another constituent. Attempts to isolate (III), araban, or AcOH from (I) failed, and the (III) is thus chemically bound to the uronic acid complex. Galactose and xylose are not formed on hydrolysis. (IV) is identical with the digalacturonic acid-*b* of Ehrlich *et al.* (A., 1926, 547), whose nomenclature is erroneous. Methylation of (IV) by HCl–MeOH and subsequent hydrolysis gives ~44% of Me methylgalacturonate (and a little ascorbic acid), the low yield being due to simultaneous decarboxylation by the acid. Determination of the CO_2 evolved by acid shows 97·07% of uronic acid in (IV) and 84—90% in (I). Furfuraldehyde is obtained in the following yields: *d*-galacturonic acid 30·9 (cf. *loc. cit.*), (I) 39·26—39·74, (II) 37·54—37·67, (IV) 36·32—36·51, (III) 85—89%; the differences for (I), (II), and (IV) are due to loss of or alteration to the combined (III). At 100° HNO_3 converts (I) into pyromucic acid, but with HNO_3 (*d* 1·5) at room temp. (I), (II), and (IV) give nitrates. That from (I) has $[\alpha]_D^{20}$ +266—277° in $COMe_2$ and indicates (η) for (I) a mol. wt. 145,000—227,000 according to the concn. and method of prep. During retting micro-organisms decompose (I) (termed pectin *A*), dissolving much and leaving an insol. pectin *B*, which with NH_4 salts yields only very little (I) and on long boiling in H_2O decomposes with dissolution (no experimental details). The raw material for prep. of (I), extracted with CH_2Cl_2 and acid, gives as ash SiO_2 0·025, $Fe_2O_3 + Al_2O_3$ 0·027, CaO 1·596, MgO 0·268, and K_2O 0·4%; there is no proof that Ca or Mg forms an integral part of the pectin. It is concluded that (I) consists of 14 galacturonic acid residues, esterified with 2 Me, 1 arabinose, and an unknown substance (not a carbohydrate). This agrees also with C and H contents and with the view that 27 OH are esterified in the nitrates (N contents), but data from the nitrates and η must be interpreted with caution. R. S. C.

Steric hindrance.—See A., 1942, I, 174.

Reaction rates of oxidation of liquid acetaldehyde.—See B., 1942, II, 89.

Reaction of nitroparaffins with aldehydes.—See B., 1942, II, 91.

Action of chlorine on mesityl oxide. D. V. Tischtschenko (*J. Gen. Chem. Russ.*, 1941, **11**, 402—404).—The action of Cl_2 on mesityl oxide gives chiefly $CH_2{:}CMe{\cdot}CHCl{\cdot}COMe$, contrary to the findings of Pauly and Lieck (A., 1900, i, 274). N. G.

Ketols and unsaturated ketones. I. Preparation of isomeric ketols and/or the corresponding unsaturated ketones by condensations involving substituted magnesium aminates. V. V. Tschelincev and A. V. Pataraia (*J. Gen. Chem. Russ.*, 1941, **11**, 461—466).—The ketone COMeR is treated with NHPhMe–MgBr and the product with a further equimol. quantity of COMeR′ to give the ketol $OH{\cdot}CMeR{\cdot}CH_2{\cdot}COR'$ (I). The *ketol*, b.p. 155°/50 mm. (R = $CMe_2{:}CH{\cdot}$) is thus prepared from mesityl oxide (II), with 12% of the *ketone*, $CMe_2{:}CH{\cdot}CMe{:}CH{\cdot}CO{\cdot}CH{:}CMe_2$, b.p. 160°/53 mm. When R and R′ were different, the ketol obtained depends on the order in which the original ketones are used. Thus (II) and COPhMe (III) give a *ketol*, m.p. 84°, in which R = $CMe_2{:}CH{\cdot}$ and R′ = Ph when (II) is used first, but a *ketol*, m.p. 79° (R = Ph and R′ = $CMe_2{:}CH$) when (III) is used first. When COMeEt (IV) and (III) are used, the use of (IV) first gives a *ketol*, b.p. 140°/10 mm., with R = Et and R′ = Ph, whereas the reverse order gives a *ketol* (R = Ph and R′ = Et), with the *ketone* $CPhMe{:}CH{\cdot}COEt$, b.p. 175—180°/47 mm. From COMePr (V) and (III), with (V) being used first, only the *ketone* $CMePr{:}CHCOPh$, b.p. 170°/32 mm., is obtained. When (III) is used first, the *ketone*, $CPhMe{:}CH{\cdot}COPr$, b.p. 147°/13 mm., results. The unsaturated ketones are derived in all cases from the expected ketols of type (I) through loss of H_2O from the ketolic OH and the adjacent CH_2. N. G.

Alkalimetric determination of amines.—See A., 1942, II, 212.

Thermal decomposition of *n*-butylamine.—See A., 1942, I, 207.

Aliphatic amines. II. Preparation and toxicity of *n*-heptylamines. M. F. W. Dunker, W. H. Hartung, and C. W. Chapman (*J. Amer. Pharm. Assoc.*, 1941, **30**, 623—625).—*n*-Heptaldoxime, m.p. 53·5—54·5°, and Me *n*-amyl, b.p. 88—90°/5—6 mm., Et Bu$^{\alpha}$, b.p. 85—105°/5 mm., and Pr$^{\alpha}$ ketoxime, b.p. 85—86°/6—7 mm., are reduced (EtOH–Na) to α-amino-, b.p. 154·5—155·5°/765 mm. (*benzamide*, m.p. 34—35°; picrate, m.p. 120—121°), β-*amino*-, b.p. 141·8—142·5°/758 mm. (*benzamide*, m.p. 68—69°; *picrate*, m.p. 97—98°; aurichloride, m.p. 77—78·5°), γ-*amino*-, b.p. 140—144°/761 mm. (*benzamide*, m.p. 89·5—90°; *picrate*, m.p. 120—121·5°), and δ-amino-heptane, b.p. 140—141°/761 mm. (*benzamide*, m.p. 108·5—109·5°; *picrate*, m.p. 165·5—166·5°), respectively. The toxicity of the four amines in mice was determined (cf. A., 1942, III, 484). F. O. H.

***N*-Dichlorocarbamates.** J. Bougault and P. Charrier (*Compt. rend.*, 1941, **213**, 310—313).—*N*-Dichlorocarbamates are almost quantitatively obtained by the action of conc. aq. NaOCl on an aq. solution of the ester acidified with H_2SO_4 or AcOH. β-*Chloro-*

ethyl N-*dichlorocarbamate* has m.p. 38°. $NCl_2{\cdot}CO_2Et$ and $CHPh{:}CH_2$ preferably in C_6H_6 yield *Et chloro-β-chloro-β-phenylethylaminoformate*, a liquid which cannot be distilled, which liberates I when treated with HI, thus permitting its iodometric determination, and is reduced ($NaHSO_3$) to *Et β-chloro-β-phenylethylaminoformate*, m.p. 50°; this is hydrolysed by Na_2CO_3 or $AgNO_3$ in aq. EtOH to *Et β-hydroxy-β-phenylethylaminoformate*, m.p. 85°, and converted by aq. 2N-NH_3 into $Ph{\cdot}[CH_2]_2{\cdot}NH{\cdot}CO_2Et$, which gives $Ph{\cdot}[CH_2]_2{\cdot}NH_2$ when heated with conc. acids at 140°. The following compounds are similarly derived from anethole and safrole but the yields are lower: *Et chloro-β-chloro-β-*m-*anisyliso**propylaminoformate*, a liquid, and *Et β-chloro-β-*m-*anisyliso**propylaminoformate*, m.p. 76°; *Et chloro-β-chloro-β-methylenedioxyphenyliso**propylaminoformate*, a liquid, and *Et β-chloro-β-methylenedioxyphenyliso**propylaminoformate*, m.p. 114°. H. W.

Aromatic sulphonic acids as reagents for amino-acids. Preparation of *l*-serine, *l*-alanine, *l*-phenylalanine, and *l*-leucine from protein hydrolysates. W. H. Stein, S. Moore, G. Stamm, C. Y. Chou, and M. Bergmann (*J. Biol. Chem.*, 1942, **143**, 121—129; cf. A., 1940, II, 365).—Solubilities in dil. HCl at 0° of the salts of 20 NH_2-acids with 22 sulphonic acids are recorded. $OH{\cdot}[CH_2]_2{\cdot}OEt$ is added in cases of the less sol. sulphonic acids. The *l-iso*leucine salt of 4-nitro-4′-methyldiphenylamine-2-sulphonic acid is much less sol. than the corresponding *l*-leucine or *l*-phenylalanine salt. Azobenzene-4-, 4-hydroxyazobenzene-4′- (**I**), 4-hydroxy-3-carboxyazobenzene-3′- and -4′- (**II**), and 2-hydroxy-5-methylazobenzene-3′-sulphonic acid (**III**), anthraquinone-1- and -2-sulphonic acid, and 5-nitroanthraquinone-1-sulphonic acid (**IV**) all form sparingly sol. salts with most of the NH_2-acids. The arginine and histidine salts of (**II**) and (**III**), and the glycine, arginine, histidine, and lysine salts of (**IV**), are of low solubility. *l*-Serine is pptd. by (**I**). An insol. NH_2-acid fraction obtained from hæmoglobin hydrolysate affords, through its 2-bromotoluene-5-sulphonate, *l*-leucine, $[\alpha]_D^{26}$ +15·5° in aq. HCl, and through its 2 : 5-dibromobenzenesulphonate, *l*-phenylalanine, $[\alpha]_D^{26}$ −34·0° in H_2O. Degummed Japanese white silk is hydrolysed (HCl), and tyrosine removed, then glycine as the 5-nitronaphthalene-1-sulphonate, *l*-alanine as the azobenzene-*p*-sulphonate, and *l*-serine, $[\alpha]_D^{26}$ −6·8° in H_2O or +13·9° in dil. HCl, as the salt of (**I**). A. T. P.

Synthesis of *d*-erythro- and *d*-threo-α-amino-βγ-dihydroxy-*n*-butyric acids. C. Niemann and P. L. Nichols (*J. Biol. Chem.*, 1942, **143**, 191—202).—The synthesis of $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(NH_2){\cdot}CO_2H$ (**I**), decomp. 215°, $[\alpha]_D^{24}$ −13·7° in H_2O (it is not a mixture), is repeated (cf. Fischer *et al.*, A., 1936, 711) and a second isomeric acid (**II**), m.p. 192—194° (decomp.), $[\alpha]_D^{24}$ +16° + H_2O, is also isolated; the two acids are d-*threo*- and d-*erythro*-α-*amino*-βγ-*dihydroxy*-n-*butyric acid*, respectively. The prefixes define the relative configuration about the two asymmetric C bearing the NH_2 and OH. (**I**) and BzCl–aq. NaOH give d-*threo*-α-*benzamido*-βγ-*dihydroxy*-n-*butyrolactone* (**III**), m.p. 210—211° (decomp.), $[\alpha]_D^{24}$ +31·3° in aq. NaOH [$NHPh{\cdot}NH_2$ at 100° in N_2 yields the n-*butyr*-(N-*phenyl*)*hydrazide* (**IV**), m.p. 169°, $[\alpha]_D^{24}$ −15·9° in C_5H_5N, −9·1° in AcOH, readily hydrolysed to (**III**)], hydrolysed by aq. HCl to (**I**). (**IV**) refluxed with aq. $CuSO_4$ gives (**III**) + (**I**). Incubation of $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(NHBz){\cdot}CO_2Na$, prepared from (**III**), with $NHPh{\cdot}NH_2$, purified papain, and cysteine hydrochloride at p_H 4·7 at 40° for 1 week gives (**IV**). (**II**) yields d-*erythro*-α-*benzamido*-βγ-*dihydroxy*-n-*butyric acid*, m.p. 135—136°, $[\alpha]_D^{24}$ −23·3° in aq. NaOH [n-*butyr*(N-*phenyl*)*hydrazide*, m.p. 203—204° (decomp.), $[\alpha]_D^{25}$ +87·8° in C_5H_5N], reconvertible by aq. HCl into (**II**), or converted by refluxing with BuOH into a 2 : 1 mixture, m.p. 135—138°, $[\alpha]_D^{24}$ −5·8° in aq. NaOH, of d-*erythro*-α-*benzamido*-βγ-*dihydroxy*-n-*butyrolactone* and (**III**). The rate of O_2 consumption in c.c. per hr. at 30° is 27·6 for (**II**) and nil for (**I**). Vals. of $[\alpha]$ for (**I**) change in a positive sense, and for (**II**) in a negative sense, with increase in acid concn. (cf. Lutz *et al.*, A., 1931, 943). All evidence supports homogeneity and configurations assigned to (**I**) and (**II**). The structure proposed for sphingosine by Klenk *et al.* (A., 1931, 829) is considered to be incorrect. A. T. P.

New hydrolysis product derived from bovine cerebral and spinal tissue. C. Niemann (*J. Amer. Chem. Soc.*, 1941, **63**, 3535—3536).—Acetylation of the mother-liquor from sphingosine sulphate (obtained from bovine cerebral or spinal tissue) gives triacetyl- and ? ON-*diacetyl*-O-*tetradecyl*-*sphingosine*, m.p. 102—102·5° (corr.), $[\alpha]_D^{26}$ −17·1° in C_5H_5N, the structure of which is indicated by analysis, absorption (catalytic) of 1·1 H_2, presence of 1 active H, mol. wt., and hydrolysis to AcOH (1 mol. readily). R. S. C.

Factors which influence oxidation of thiol groups. M. L. Anson (*J. Gen. Physiol.*, 1942, **25**, 355—367).—Oxidation of the SH groups of cysteine and denatured ovalbumin (**I**) by Folin's uric acid reagent is inhibited by CN′. In presence (but not in absence) of $CuSO_4$, the reagent and $K_3Fe(CN)_6$ oxidise cysteine at p_H 8. The reagent also oxidises the SH of denatured (**I**) in neutral solution containing $CO(NH_2)_2$ but does not oxidise it in presence of long-chain alkyl sulphate (**II**) or in absence of denaturing agent. In absence of denaturing agent, the reagent oxidises SH of (**I**) partly hydrolysed by pepsin but not those of neutral denatured but unhydrolysed (**I**). $K_3Fe(CN)_6$ oxidises SH of neutral denatured (**I**) even in presence of (**II**) and also, if aggregation be prevented, in absence of denaturant. In acid solution, $K_3Fe(CN)_6$ does not completely oxidise SH of denatured (**I**). Denaturants, in the order guanidine hydrochloride > $CO(NH_2)_2$ > (**II**), increase the extent of oxidation. SH groups of (**I**) digested with pepsin are more completely oxidised by $K_3Fe(CN)_6$ in presence of (**II**) at p_H 4·8 than are those of denatured but undigested (**I**). W. McC.

Optical rotation of *l*-cystine. G. Toennies (*J. Biol. Chem.*, 1942, **143**, 75).—$[\alpha]_D^{31\cdot5}$ should replace $[\alpha]_{Hg}^{31\cdot5}$ in certain cases in a previous paper (A., 1936, 320). A. T. P.

Synthesis of *ll*-*S*-(β-amino-β-carboxycthyl)homocysteine and the replacement by it of cystine in the diet. V. du Vigneaud, G. B. Brown, and J. P. Chandler (*J. Biol. Chem.*, 1942, **143**, 59—64; cf. A., 1941, II, 122).—*l*-Homocysteine, aq. KOH, and $l\text{-}CH_2Cl{\cdot}CH(NH_2){\cdot}CO_2H$,HCl (in N_2) at 50° for 3 hr., then overnight at 0° (at p_H 6·5), afford ll-S-(*β-amino-β-carboxyethyl*)*homocysteine*, darkens at 270°, decomp. 312°, $[\alpha]_D^{20}$ +23·7° in N-HCl (NN-Bz_2 derivative, m.p. 229°), which can serve in place of cystine in the diet for support of growth of animals. A. T. P.

Manufacture of urea.—See B., 1942, II, 94.

βγ- and γδ-Dimethylthiosemicarbazide. E. Cattelain (*Compt. rend.*, 1941, **213**, 308—310).—MeI and α-$NH_2{\cdot}NMe{\cdot}CS{\cdot}NH_2$-δ give non-cryst. βγ-dimethylthiosemicarbazide hydriodide, the structure of which is proved by its conversion by $CH_2Ph{\cdot}CO{\cdot}CO_2H$ into 5-*keto*-3-*methylthiol*-6-*benzyl*-1 : 2 : 4-*triazine*, m.p. 116·5°. *Benzald-*, m.p. 187°, and *anisald-*, m.p. 195°, *-βγ-dimethylthiosemicarbazone hydriodide* are described. Similarly $NH_2{\cdot}NH{\cdot}SH{:}NMe$ and MeI afford *γδ-dimethylthiosemicarbazide hydriodide*, m.p. 160·5°, transformed by $CH_2Ph{\cdot}CO{\cdot}CO_2H$ into the corresponding *γδ-dimethylthiosemicarbazone*, m.p. 154·5°, which cannot be cyclised. The *γδ-dimethylthiosemicarbazone hydriodides* of PhCHO and *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$ have m.p. 162° and 139—140° respectively. H. W.

Hydrogenation of nitriles.—See B., 1942, II, 93.

Preparation of α-chloroacrylonitrile.—See B., 1942, II, 93.

Manufacture of chloropropionitriles.—See B., 1942, II, 94.

Manufacture of ααβ-trichloropropionitrile.—See B., 1942, II, 94.

Photolysis of azomethane in presence of hydrogen.—See A., 1942, I, 209.

II.—SUGARS AND GLUCOSIDES.

Substituted semicarbazones. III. Attempted application to the determination of glucose.—See A., 1942, II, 212.

Reaction between glucose and iodine in alkaline medium. Effect of neutral salts.—See A., 1942, I, 207.

Caramelisation of fructose and fructosans by the action of heat. H. Colin and H. Belval (*Bull. Assoc. Chim. Sucr.*, 1941, **58**, 281—292).—The work of Gélis and of Pictet on the action of heat on sucrose and fructose respectively, and the properties of (poly-) fructosans (**I**), are reviewed. Fructose on heating yields fructosan (**II**). Dry heating of (**I**) (*e.g.*, triticosan, graminosan) causes a progressive decrease in lævorotation, which may eventually become positive, and there is simultaneous development of reducing properties. Normal hydrolysis being impossible, it is assumed that fragmentation of the mols. takes place, giving re-oriented products of rotation > that of (**II**) and containing a marked proportion of aldose groupings susceptible of oxidation by I. I. A. P.

Detection of lactose and maltose by means of methylamine. W. R. Fearon (*Analyst*, 1942, **67**, 130—132).—1% aq. solutions of lactose and maltose on boiling for 30 sec. with a few drops of 5% aq. NH_2Me,HCl give a yellow colour slowly changing to carmine when made alkaline with 20% NaOH and allowed to cool. NH_2Et and $NH_2{\cdot}[CH_2]_2{\cdot}OH$ also give the same reaction. Many other sugars, carbohydrates, and sugar decomp. products do not give a positive reaction but reducing saccharides give a deepening yellow colour. Lactose in concns. >0·05% and NH_2Me >0·05% are detectable but reducing sugars inhibit the reaction. S. B.

Glucoside from the leaves of *Rhododendron flavum*, Don. A. G. Schwartzman (*J. Gen. Chem. Russ.*, 1941, **11**, 467—470).—The glucoside (**I**) $C_{21}H_{20}O_{12}.H_2O$, m.p. 245—246°, isolated according to the method of Hattori *et al.* (cf. A., 1937, III, 503), is of the flavone type. Methylation (CH_2N_2), followed by hydrolysis, gives 5 : 7 : 3′ : 4′-tetramethylquercetin. (**I**) is therefore quercetin-3-glucoside (*iso*quercctrin); the leaves used had been kept for a long period prior to the investigation, and (**I**) may have been derived by enzymic hydrolysis during storage from the glucoside rutin. N. G.

Starch. XIX. Degradation of amylose by amylase. K. H. Meyer and P. Bernfeld (*Helv. Chim. Acta*, 1941, **24**, 359—369E).—A study of the action of malt α-amylase on amylose leads to the conclusion that all glucosidic linkings whatsoever are destroyed without distinction by the enzyme with the exception of the terminal linkings which are much more slowly attacked. The large

fragments are degraded more rapidly than the small fragments. As it does not possess terminal glucosidic linkings maltotriose is only very slowly converted into maltose and glucose. H. W.

New crystallised fraction of starch and the *X*-ray diagrams of starch. E. Wiegel (*Z. physikal. Chem.*, 1941, **A**, **188**, 137—159).—A new cryst. fraction of starch has been obtained from many kinds of natural starch by cooling a hot solution in 30% EtOH. It is cryst. amylose, and gives an *X*-ray diagram resembling the so-called *V*-spectrum, but sharper. After thorough drying this changes to a different but equally sharp diagram, the original diagram slowly reappearing on exposure to moist air. The relation between the various *X*-ray diagrams of starch is discussed. F. J. G.

High-temperature modification of cellulose (cellulose IV). K. Hess and H. Kiessig (*Z. physikal. Chem.*, 1941, **B**, **49**, 235—244).—When cellulose preps., of which the lattice has been distorted by spinning, are heated in glycerol to 250°, a modification (cellulose IV) is obtained, of which the lattice dimensions agree with those of the transformation product obtained by treatment of mercerised cotton threads in H_2O or glycerol at 250°. Cellulose IV has *a* 8·14, *b* 10·3, *c* 7·90 A., β 90°, whilst natural cellulose has *a* 8·23, *b* 10·3, *c* 7·84 A., β 84°. The vol. of the elementary cell is 662 A.^{3} in each case. This modification does not occur naturally. A. J. M.

Substituted native cellulose and regenerated cellulose. R. Haller and A. Heckendorn (*Helv. Chim. Acta*, 1941, **24**, 85—92E).—Details are given for the prep. of cellulose cyanurate (**I**) and allylcellulose (**II**). After some time (**I**) swells markedly in $(CH_2{\cdot}NH_2)_2$-$Cu(OH)_2$ (**III**) but the spherical enlargements characteristic of native cellulose (**IV**) appear only sporadically. In KI_3 (**I**) is coloured yellow-brown and addition of H_2SO_4 (*d* 1·53) does not immediately cause blue specks, which ultimately fill the whole fibre, leaving residues of esterified layers. In (**III**), (**II**) exhibits movements due to tension during swelling but the pearl-like enlargements are never observed. Alkaline azo-blue does not colour (**II**) for a long time. With I followed by H_2SO_4 green and finally blue specks are ultimately formed. In (**I**) ester formation therefore is restricted to the outer layers whereas in (**II**) etherification affects the whole fibre. The refractory behaviour of (**I**) and (**II**) towards substantive cotton dyes is relative and a function of the degree of dispersion of the dye in aq. solution. A pronounced surface action is involved. It is advocated that on the basis of definite reactions a distinction should be drawn between regenerated celluloses obtained from esters in which the fibre structure is preserved and products which involve a complete disorganisation of (**IV**) and subsequent pptn. (**IV**) adsorbs only minute amounts of Au from 1% $AuCl_3$ and the fibres become only pale silver-grey when pressed between filter-paper and then placed in a solution of $NHPh{\cdot}NH_2$,HCl (**V**). Esterified (**IV**) [*e.g.*, (**I**)] adsorbs considerable amounts of Au and the product gives a dark grey to black colour in (**V**). In H_2SO_4 the kernel of (**I**) rapidly becomes disorganised and the much more resistant esterified outer layer of the fibre remains. Cellulose obtained by hydrolysis of an ester with NaOH retains the affinity for Au almost unimpaired. The hydrolysed fibre is coloured dark grey and the external layer shows a marked resistance to H_2SO_4. H. W.

III.—HOMOCYCLIC.

High-temperature alkylation of aromatic hydrocarbons.—See B., 1942, II, 89.

Synthesis of toluene.—See B., 1942, II, 94.

Ozonisation of *o*-xylene and 1 : 2 : 4-trimethylbenzene. J. P. Wibaut and P. W. Haagman (*Science*, 1941, **94**, 49).—The proportions of dimethylglyoxime, methylglyoxime, and glyoxime formed from the products of ozonisation of *o*-xylene and of 1 : 2 : 4-$C_6H_3Me_3$ indicate that the resonating Kekulé forms each contribute 50% to the structure of the hydrocarbon. E. R. R.

Manufacture of styrene.—See B., 1942, II, 94.

Dipole moments of gallium chloride and its molecular compounds.—See A., 1942, I, 165.

Sesquiterpenes. L. Constitution and colour of azulene. P. A. Plattner (*Helv. Chim. Acta*, 1941, **24**, 283—294E).—The chemically determined formula of azulene (**I**) with five continuous conjugated double linkings completely explains the optical behaviour if the hydrocarbon is regarded as a mesomeric system. The absorption spectra of the azulenes fall into three classes. The first comprises 1-methyl-, 1 : 4 : 7-trimethyl-, cham-, guai-, 1 : 4-dimethyl-, 4-methyl-, and 4 : 8-dimethyl-azulene and (**I**). All have nearly identical spectra which are sometimes shifted by definite amounts relatively to one another. In all cases there is a nearly const. difference of ~730 cm.$^{-1}$ between λ of the individual bands of the same spectrum. The distribution of the intensities of the bands in the individual series is the same in all cases, the first, third, and fifth bands being relatively the strongest. The displacement due to Me in varying nos. and positions is discussed. The second group is composed of azulenes substituted at $C_{(2)}$; the spectrum differs completely from that of (**I**) and the reason is not immediately apparent. 2-Methylazulene has a many-banded spectrum with well marked bands; 2-*iso*propyl- and 2-ethyl-azulene appear similar. Vetivazulene (4 : 8-dimethyl-2-*iso*propylazulene) has few, flat bands and is closely imitated by Se-guaiazulene, which is probably therefore a 2 : 4 : 7-derivative. The third group contains only 5-methyl- and 1 : 2-dimethyl-azulene. Possibly the former can be classed in the first group but the intensities are very different. The material is here too scanty for generalisations. H. W.

Bromofluoranthenes. R. Tobler, T. Holbro, P. Sutter, and W. Kern (*Helv. Chim. Acta*, 1941, **24**, 100—109E).—4-Bromofluoranthene, m.p. 110°, is obtained in small yield by the monobromination of fluoranthene (**I**) but is better prepared by dehydrogenation of 4-bromo-5 : 6 : 7 : 8-tetrahydrofluoranthene by chloranil in boiling xylene. 4 : 11(?)-Dibromofluoranthene (**II**), m.p. 205°, is obtained in 60—62% yield by the action of Br on (**I**) in $PhNO_2$ at room temp. The position of the Br atoms in (**II**) is not finally established; one is at $C_{(4)}$ and the second cannot be at $C_{(5)}$, $C_{(6)}$, or $C_{(7)}$ since bromination of 5 : 6 : 7 : 8-tetrahydrofluoranthene in CCl_4 gives a *dibromo*-5 : 6 : 7 : 8-*tetrahydrofluoranthene*, m.p. 166°, dehydrogenated to (**II**). Of the remaining possibilities $C_{(11)}$ is considered most probable since sulphonation yields a 4 : 11-disulphonic acid. Attempts to synthesise (**II**) were unsuccessful. Successive addition of $Et_2C_2O_4$ and 2 : 7-dibromofluorene (**III**) to KOEt in xylene gives the *K* salt, decomp. 255° (and similarly the *Na* salt), of *Et* 2 : 7-*dibromofluorene*-9-*oxalate*, m.p. 181°. Similarly (**III**), KOEt, and HCO_2Et give 2 : 7-*dibromofluorene*-9-*aldehyde* (or 2 : 7-*dibromo*-9-*hydroxymethylenefluorene*), m.p. 182°, which shows no tendency towards polymerisation; its *anil*, m.p. 215° (decomp.), and unstable *phenylhydrazone* are described. Successive additions of *o*-NHAc·C_6H_4·CHO and (**III**) to NaOEt in EtOH at 50—60° lead to 2 : 7-*dibromo*-9-*o-acetamidobenzylidenefluorene*, m.p. 247°, hydrolysed by conc. HCl at 180—185° to the *o*-NH_2-compound, m.p. 136°, which is converted by H_2SO_4 and *iso*-$C_5H_{11}{\cdot}O{\cdot}NO$ in C_6H_6 into 4 : 11-*dibromo*-5 : 6-*benzfluoranthene*, m.p. 216°. This is reduced by Na–Hg and boiling 96% EtOH to *octahydro*-5 : 6-*benzfluoranthene*, m.p. 139—140°, dehydrogenated to 5 : 6-*benzfluoranthene*, m.p. 167°. Addition of Br to (**II**) in $PhNO_2$ containing I at 90—95° gives *tribromofluoranthene*, m.p. 204—205°. If the proportion of Br is increased and the temp. raised to 120—125° the product is *tetrabromofluoranthene*, m.p. 312°. H. W.

***N*^{1}*N*^{1}'-Alkylidenedisulphanilamides.**—See B., 1942, III, 141.

Phototropic aminoazo-dyes. L. von Mechel and H. Stauffer (*Helv. Chim. Acta*, 1941, **24**, 151—161E).—The following derivatives of 4-aminoazobenzene are obtained by coupling the necessary azo-compound with aniline-ω-methanesulphonic acid in presence of $NaHCO_3$, salting out and collecting the azo-dye, and removing $MeSO_2$ by warm dil. NaOH: 3'-, m.p. 89—91°, and 4'-*methyl*-, m.p. 144—146°; 3'-, m.p. 92—93°, and 4'-, m.p. 145—147°, -*methoxy*-; 2'- (**I**), m.p. 144—146°, 3'-, m.p. 96—97°, and 4'-, m.p. 147—148°, -*chloro*-; 2'- (**II**), m.p. 100—101°, 3'-, m.p. 212—213°, and 4'- (**III**), m.p. 210—212°, -*nitro*-; 3'- (**IV**), m.p. 129—130°, and 4'- (**V**), m.p. 207—208°, -*methanesulphonyl*-2-*methyl*-, m.p. 64—66°; 2 : 2'-, m.p. 106—107°, and 2 : 4'-, m.p. 124—126°, -*dimethyl*-; 2'-*methoxy*-2-*methyl*-, m.p. 131—132°; 4'-*ethoxy*-2-*methyl*-, m.p. 107—109°; *Na* 4-*amino*-2'-*methanesulphonylazobenzenc*-ω-*methanesulphonate* (**II**), m.p. 221° (decomp.). The following derivatives of 4-dimethylaminoazobenzene, m.p. 117°, are described: 2'-, m.p. 65—66°, 3'-, m.p. 119—120°, and 4'-, m.p. 168—169°, -*methyl*; 2'-*methoxy*-, m.p. 91—92°; 4'-*ethoxy*-, m.p. 152—153°; 2'-, m.p. 108—109°, 3'-, m.p. 109—110°, and 4'- (**VII**), m.p. 152—153°, -*chloro*-. Of these, (**I**) to (**V**) are not phototropic and (**VI**) only slightly, so that negative substituents appear to hinder this property. The parent dye, (**III**), and (**VII**) have been particularly investigated. For these, only the rays of the extreme visible violet are active; ultra-violet and blue to infra-red are without action. The change is inhibited at −180° and −80° but expedited at 65°; the reverse change is inhibited at −180°. Phototropy is therefore due not to a simple modification of the electronic structure of the dye but to a change involving heavier particles. The dyes are phototropic on acetyl-, ethyl-, and benzyl-cellulose but not on cellulose nitrate, paper, celluloid, or fatty acid. The light reactions appear to occur exclusively in solution. The absorbtion curves of the dyes in EtOH and in a cellulose acetate film are recorded. Measurements of the rate of transformation give little hope of isolation of the labile form. H. W.

Action of nitric oxide on nitroso-compounds. A. N. Nesmejanov and S. T. Joffe (*J. Gen. Chem. Russ.*, 1941, **11**, 392—401; cf. A., 1939, II, 543).—Interaction between NO and the following Ar·NO gives, as suggested by Bamberger (A., 1897, 508), the corresponding $ArN_2{\cdot}NO_3$: *p*-NO·C_6H_4·$NAlk_2$, *p*-NO·C_6H_4·NHAlk, *p*-NO·C_6H_4·NAlk·NO (*p*-group only reacts), 1-$C_{10}H_7$·NO, 4-nitroso-antipyrine, and 3-nitrosocarbazole. Under the conditions of the Bamberger reaction, the following did not react with NO: aliphatic and *N*-NO-compounds, ψ-nitrols, oximino-compounds, *p*-NO·C_6H_4·NMe_2 (cf. above), *p*-NO·C_6H_4·ONa, *o*-$C_6H_4(NO)_2$, 4 : 1 : 3-$NO{\cdot}C_6H_3(OH)_2$, 1 : 2-NO·$C_{10}H_6$·OH, and 3-nitroso-2 : 6-diammopyridine. The non-reactivity is probably due to the existence of

these compounds in quinonoid forms. Bamberger's suggestion (A., 1918, i, 353) that NO adds to the double linking of the NO-group with a subsequent intramol. change to the $ArN_2 \cdot NO_3$ was confirmed. The following complex diazonium *salts* are new: *p*-$N_2Cl \cdot C_6H_4 \cdot NHMe,HCl,HgCl_2$, m.p. 144—145° (decomp.); *p*-$N_2Cl \cdot C_6H_4 \cdot NHEt,HCl,HgCl_2$, m.p. 126° (decomp.); 5 : 1 : 2-$N_2Cl \cdot C_6H_3Me \cdot NHMe,HCl,SbCl_3$, m.p. 124° (decomp.); (*p*-$N_2Cl \cdot C_6H_4 \cdot NMe \cdot NO)_2,PtCl_4$, m.p. 145—147° (decomp.) [corresponding *N*-Et *salt* has m.p. 135° (decomp.)]. 4-*Hydroxy*-2-*methyl*-5-iso*propylbenzenediazonium nitrate* has m.p. 100° (decomp.).

N. G.

Production of diazoamino-compounds.—See B., 1942, II, 184.

Halogenation of fatty acids. III. Reaction between alkyl halides and phenols. Formation of long-chain alkyl ethers. T. N. Mehta, V. S. Mehta, and V. B. Thosar (*J. Indian Chem. Soc., Ind. Ed.*, 1941, **4**, 170—174).—The following *ethers* are prepared from ArOH and AlkBr in boiling 0·5*N*-EtOH–KOH: β-$C_{10}H_7$ *heptadecyl*, m.p. 70—71°, *pentadecyl*, m.p. 66—67°, *tridecyl*, m.p. 61—62°, and *undecyl*, m.p. 55—56°, *pyrocatechol diheptadecyl*, m.p. 62°, *dipentadecyl*, m.p. 56—57°, *ditridecyl*, m.p. 50—51°, and *diundecyl*, m.p. 43°, *resorcinol diheptadecyl*, m.p. 75°, *dipentadecyl*, m.p. 68—69°, *ditridecyl*, m.p. 64—65°, and *diundecyl*, m.p. 56°, and *quinol diheptadecyl*, m.p. 91°, *dipentadecyl*, m.p. 85°, *ditridecyl*, m.p. 81°, and *diundecyl*, m.p. 76°. The Br_2-derivatives (Br in $CHCl_3$) of these have m.p. 73°, 68°, 62—63°, 57—58°, 64—65°, 58—59°, 56°, 46°, 68—69°, 58°, 53°, 48°, 82—83°, 78°, 75—76°, and 72°, respectively. $C_6H_4(OH)_2$ with less AlkBr give monoalkyl ethers: *pyrocatechol heptadecyl*, m.p. 43°, *resorcinol heptadecyl*, m.p. 62°, and *pentadecyl*, m.p. 52—53°, and *quinol heptadecyl*, m.p. 91—92°, *pentadecyl*, m.p. 85—86°, *tridecyl*, m.p. 82°, and *undecyl ether*, m.p. 78°, which with PhN_2Cl and EtOH–KOH give *azo-compounds*, m.p. 53—54°, 100—101° (*bisazo-compound*), 93—94° (*bisazo-compound*), 68°, 60—61°, 56°, and 50°, respectively.

A. Li.

Formaldehydesulphoxylate derivatives of diphenyl sulphides, disulphides, sulphoxides, and sulphones.—See B., 1942, II, 185.

Derivatives of 4 : 4′-diaminodiphenyl sulphone.—See B., 1942, II, 184.

Resolution of *dl*-ephedrine.—See B., 1942, III, 142.

Grignard reactions with halogenoalkylamines. A. Marxer (*Helv. Chim. Acta*, 1941, **24**, 209—225E).—$NEt_2 \cdot [CH_2]_2 \cdot Cl$ does not react with Mg under the usual conditions. $NEt_2 \cdot [CH_2]_3 \cdot Cl$ (**I**) reacts vigorously with activated Mg but reaction soon stops by reason of a coat which forms around the metal. This happens also when a mixture of halide and CO-compound is added to the metal. Satisfactory results are secured when (**I**) is added to Mg containing some Gilman's Mg–Cu alloy which has been activated with I and brought into brisk reaction with EtBr. The reaction must not be allowed to subside, further EtBr being added if necessary towards the close. The aldehyde or ketone is immediately added in small portions to the mixture warmed to 45°, addition being so regulated that the exothermic action is continuous. In this manner the Mg compound is kept in solution until the change is almost complete. Reaction is satisfactory with aromatic aldehydes and ketones but less so with the corresponding aliphatic compounds or with fatty aromatic or hydroaromatic ketones; in these latter cases it appears advantageous to use a halogenoalkylamine with a higher alkyl residue. The conversion of $Cl \cdot [CH_2]_3 \cdot Br$ into (**I**), 1-γ-chloropropylpiperidine (**II**), $NMe_2 \cdot [CH_2]_3 \cdot Cl$ (**III**), and $NBu^{\alpha}_2 \cdot [CH_2]_3 \cdot Cl$ (**IV**) is described. The following compounds are derived from (**I**): *diphenyl-γ-diethylaminopropylcarbinol*, an oil (*hydrochloride*, m.p. 179—179·5°), converted by boiling Ac_2O into δ-diethylamino-αα-diphenyl-Δ$^{\alpha}$-butene (*hydrochloride*, m.p. 126—128°), which is reduced (H_2–Rupe Ni in EtOH at room temp.) to δ-*diethylamino-αα-diphenylbutane*, b.p. 130—132°/0·08 mm.; *phenyl-γ-diethylaminopropylcarbinol*, b.p. 108—111°/0·03 mm. (very hygroscopic hydrochloride; *benzoate hydrochloride*, m.p. 154—156°; acetate, an oil, and its *hydrochloride*, m.p. 120—123°; *phenylurethane hydrochloride*, m.p. 155—156°), oxidised by CrO_3 in AcOH to *Ph γ-diethylaminopropyl ketone*, b.p. 102—104°/0·06 mm. (*hydrochloride*, m.p. 127—130°), also obtained (Grignard) from PhCN; *phenylmethyl-γ-diethylaminopropylcarbinol*, b.p. 106—110°/0·07 mm. (hydrochloride, m.p. 133—134°); α-*naphthyl-γ-diethylaminopropylcarbinol*, b.p. 158—164°/0·07 mm., m.p. 59—62° (non-cryst. acetate and its *hydrochloride*, m.p. 132—155°); p-*anisyl-γ-diethylaminopropylcarbinol*, b.p. 142°/0·15 mm.; 3 : 4-*methylenedioxyphenyl-γ-diethylaminopropylcarbinol*, b.p. 136—142°/0·07 mm. (very hygroscopic hydrochloride; *benzoate hydrochloride*, m.p. 118—120°), converted by BzCl in PhMe at 145° into δ-diethylamino-α-3 : 4-methylenedioxyphenyl-Δ$^{\alpha}$-butene, an oil (*hydrochloride*, m.p. 158—160°); 3 : 4-*dimethoxyphenyl-γ-diethylaminopropylcarbinol*, b.p. 155—161°/0·07 mm. (*hydrochloride*, m.p. 128—132°); 2-*furyl-γ-diethylaminopropylcarbinol*, b.p. 88°/0·07 mm. (**II**) yields the following: diphenyl-γ-piperidinopropylcarbinol, an oil (*hydrochloride*, m.p. 212—214°); *phenyl-γ-piperidinopropylcarbinol*, b.p. 131—133°/0·06 mm. (*hydrochloride*, m.p. 109—111°); p-*anisyl-γ-piperidinopropylcarbinol*, b.p. 153—158°/0·08 mm., m.p. 53—56° (very hygroscopic hydrochloride); 3 : 4-*methylenedioxyphenyl-γ-piperidinopropylcarbinol*, b.p. 168—170°/0·08 mm., m.p. 71—71·5° (hydrochloride, m.p. 132—134°). The following are derived from (**III**): *phenyl-γ-dimethylaminopropylcarbinol*, b.p. 106·5°/0·07 mm., m.p. 45—48°; 3 : 4-*methylenedioxyphenyl-γ-dimethylaminopropylcarbinol*, b.p. 162·5—164°/? mm. (**IV**) yields the following: *phenyl-γ-dibutylaminopropylcarbinol*, b.p. 136°/0·1 mm.; 1-*γ-dibutylaminopropylcyclohexanol*, b.p. 118°/0·1 mm. (hydrochloride, m.p. 134—136°); diphenyl-γ-dibutylaminopropylcarbinol, an oil (*hydrochloride*, m.p. 158—159° after softening at 151°). *Phenyl-ε-diethylaminoamylcarbinol* has b.p. 124—127°/0·05 mm.

H. W.

Vinylene homologues of triphenylmethane dyes. R. Wizinger and G. Renckhoff (*Helv. Chim. Acta*, 1941, **24**, 369—388E).—$(NMe_2 \cdot C_6H_4)_2C{:}CH_2$ (**I**) and *p*-$NMe_2 \cdot C_6H_4 \cdot CHO$ in AcOH–Ac_2O containing 70% $HClO_4$ at 100° yield *hexamethyltriaminotriphenylvinylcarbenium perchlorate*, $[(NMe_2 \cdot C_6H_4)_2C \cdot CH{:}CH \cdot C_6H_4 \cdot NMe_2]ClO_4$, decomp. ~175°. Similarly (**I**) and *p*-$NEt_2 \cdot C_6H_4 \cdot CHO$ afford *aa-tetramethyldiaminodiphenyl-γ-diethylaminophenylvinylcarbenium perchlorate*, decomp. ~145°. α-*Phenyl-aγ-tetramethyldiaminodiphenyl-* and α-*phenyl-α-dimethylaminophenyl-γ-diethylaminophenyl-vinylcarbenium perchlorate* are obtained similarly. Methylxanthylium perchlorate (**II**) and the requisite aldehyde give the following *-xanthylium perchlorates*: 9-*styryl-*, decomp. 188—190°; 9-*methoxystyryl-*, decomp. 187°; 9-*dimethylaminostyryl-*, decomp. 190—192°; 9-*diethylaminostyryl-*, decomp. 175—178°. (**I**) is converted by $NMe_2 \cdot C_6H_4 \cdot COPh$ and $POCl_3$ at 100° followed by $NaClO_3$, AcOH, and NaOAc into *γ-phenyl-aaγ-hexamethyltriaminotriphenylvinylcarbenium perchlorate*, decomp. 203°. Similar condensations lead to the following *-vinylcarbenium perchlorates*: *γγ-diphenyl-aa-tetramethyldiaminodiphenyl-*, decomp. 186—188°; *aγ-diphenyl-aγ-tetramethyldiaminodiphenyl-* (**III**), decomp. 193—195°; *aaγγ-octamethyltetra-aminotetraphenyl-*, decomp. 240°; *aaγγ-tetra-anisyl-*, decomp. 155°. The following *-vinylxanthylium perchlorates* result similarly: *diphenyl-*, decomp. 179°; *phenylanisyl-*, decomp. 152—155°; *dianisyl-* (**IV**), decomp. ~155°; *tetramethyldiaminodiphenyl-*, decomp. ~150°. (**II**), xanthone, and PCl_5 at 100° give *dixanthenomonomethine*, decomp. ~215°. Condensation of the substituted ethylene with the requisite aldehyde in an acid medium or treatment of the necessary dye salt with NaOAc + AcOH or C_5H_5N gives the following *-allenes*: γ-phenyl-αα-dianisyl-, m.p. 188°; phenylxanthylene-, m.p. 242°; diphenylxanthylene-, m.p. 205°; *γ-phenyl-aa-tetramethyldiaminodiphenyl-*, m.p. 192° (decomp.); *γ-anisyl-aa-tetramethyldiaminodiphenyl-*, m.p. 209°; *γ-methylenedioxyphenyl-aa-tetramethyldiaminodiphenyl-*, m.p. 221—222° (decomp.); *aaγ-hexamethyltriaminotriphenyl-*, m.p. 213° (decomp.); *aa-tetramethyldiaminodiphenyl-γ-diethylaminophenyl-*, m.p. 188°; *anisylxanthylene-*, m.p. 195°; *tetra-anisyl-*, m.p. 127°; *phenylanisylxanthylene-*, m.p. 173°; *dianisylxanthylene-*, m.p. 124°; *dixanthylene-*, m.p. 255—256°. (**III**) and piperidine at room temp. afford *aγ-diphenyl-aγ-tetramethyldiaminodiphenylallyl alcohol*. (**IV**) is converted by short treatment with boiling AcOH into 6-*methoxy*-3-*anisyl*-1 : 1-*xanthenoindene*, m.p. 178°.

H. W.

Reaction of carboxyhydroxymethylamides and their functional derivatives with hydroxy-compounds. O. Albrecht, J. Frei, and R. Sallmann (*Helv. Chim. Acta*, 1941, **24**, 233—247E).—Model experiments show that the ·NH·CH_2·OH group of certain substituted amides is readily etherified when heated with alcohols in the presence of acids. Reaction appears general and it is probable that the thermal decomp. of such compounds, used in rendering textiles fast to washing, involves the formation of O-bridges with OH of the textile. $CH_2Cl \cdot CO \cdot NH \cdot CH_2 \cdot OH$ and $CH_2Ph \cdot OH$ undergo a complex reaction in the presence of a little HCO_2H at 115—120° which leads to $(CH_2Cl \cdot CO \cdot NH)_2CH_2$ and, after treatment with C_5H_5N, the *pyridinium* salt of *chloroacetbenzyloxymethylamide* (**I**), m.p. 170—172°, and an unidentified *compound*, m.p. 237—239°. (**I**) is also obtained from the pyridinium salt of $CH_2Cl \cdot CO \cdot NH \cdot CH_2 \cdot OH$, $CH_2Ph \cdot OH$, and a little HCO_2H at 115—120°, and from the additive product of C_5H_5N with chloroacetamidomethyl*iso*thiocarbamide hydrochloride and $CH_2Ph \cdot OH$. Schemes of reaction are proposed. The derivatives of $CH_2Cl \cdot CO \cdot NH_2$ described above give ill-defined, non-cryst. products with glucose which afford little promise of the isolation of individuals. *o*-$C_6H_4Cl \cdot CH{:}CH \cdot CO \cdot NH_2$, paraformaldehyde, and C_5H_5N at 110—115° give *o-chlorocinnamhydroxymethylamide* (**II**), m.p. 107—109°, converted by $CS(NH_2)_2$ in MeOH containing HCl into *o-chlorocinnamamidomethyliso*thiocarbamide *hydrochloride* (**III**), m.p. 159—160° (decomp.), which rapidly decomposes in H_2O with separation of *o*-$C_6H_4Cl \cdot CH{:}CH \cdot CO \cdot NH_2$. (**II**) is converted by $CH_2Ph \cdot OH$ and a little HCO_2H at 110—120° into *CH_2Ph o-chlorocinnamamidomethyl ether*, m.p. 105—107°, also obtained from (**III**), $CH_2Ph \cdot OH$, and NaOAc in H_2O at 40—50° and then at 100° (H_2O-free). Definite products have not been obtained from (**II**) and glucose.

H. W.

Preparation of basic esters of substituted acetic acids. II. K. Hoffmann (*Helv. Chim. Acta*, 1941, **24**, 36—40E).—Gradual addition of *cyclo*hexylphenylacetic acid (**I**) to fuming HNO_3 at −10° to −15° gives cyclo*hexyl*-p-*nitrophenylacetic acid* (**II**), m.p. 156—158°. The *Me* ester, m.p. 82—83°, obtained by nitration of the Me ester of (**I**) at −20° to −25°, is oxidised [HNO_3 (*d* 1·0) at 140°] to *p*-

$NO_2{\cdot}C_6H_4{\cdot}CO_2H$ and is reduced (H_2–Ni on clay–abs. EtOH at room temp.) to *Me* cyclo*hexyl*-p-*aminophenylacetate* (**III**), b.p. 165—168°/0·6 mm., m.p. 72—73°. Agitation of (**II**) with $Cl{\cdot}[CH_2]_2{\cdot}NEt_2$ (**IV**) and K_2CO_3 in EtOAc and treatment of the product with dry HCl leads to *β-diethylaminoethyl* cyclo*hexyl*-p-*nitrophenylacetate hydrochloride*, m.p. 176—178°, catalytically reduced (PtO_2 in AcOH at room temp.) to *β-diethylaminoethyl* cyclo*hexyl*-p-*aminophenylacetate hydrochloride* (**V**), m.p. 156—159°. (**III**) and (**IV**) in boiling PhMe afford *Me* cyclo*hexyl*-p-*β-diethylaminoethylaminophenylacetate* (**VI**), b.p. 110—116°/0·2 mm. (*hydrochloride*). Introduction of NH_2 into the mol. of trasentin *H* (**VII**) increases the likeness to atropine but diminishes the papaverine-like action. Unlike (**VII**), (**V**) has no anæsthetising action in 1% solution. (**VI**) is more poisonous but otherwise less active than (**VII**). H. W.

2 : 2 : 4-Trimethyl-Δ³-*cyclo*hexenecarboxylic acid : its formation from *l*-Δ³-carene-5 : 6-epoxide. A. R. Penfold and J. L. Simonsen (*J.C.S.*, 1942, 206—209; cf. A., 1940, II, 219).—The acid, $C_{10}H_{16}O_2$ (**I**), formed (A., 1939, II, 514) by the action of KOH–EtOH on *l*-Δ³-carene-5 : 6-epoxide is 2 : 2 : 4-*trimethyl*-Δ³-cyclo*hexenecarboxylic acid*. (**I**) and O_3 in MeOAc at 0° afford a liquid acid (**II**), which yields a *semicarbazone* (**III**), $C_{11}H_{17}O_3N_3$, decomp. 252°, and with NaOH–NaOBr gives *β*-methylpentane-*βγε*-tricarboxylic acid and 5 : 5-*dimethyl*-Δ³-cyclo*pentene*-1 : 3-*dicarboxylic acid* (**IV**), m.p. 198—199°, $[\alpha]_{5461}$ −15° in $COMe_2$ (with O_3 gives *β*-methylbutane-*βγδ*-tricarboxylic acid). (**II**) is formulated as $Ac{\cdot}[CH_2]_2{\cdot}CH(CO_2H){\cdot}CMe_2{\cdot}CHO$ and it is suggested that in the formation of (**IV**) cyclisation to 3-acetyl-5 : 5-dimethyl-Δ³-cyclopentenecarboxylic acid [semicarbazone = (**III**)] precedes oxidation. $CHNa(CO_2Et)_2$ and Et *γ*-bromo-*αα*-dimethylglutarate in EtOH afford *Et β-methylpentane-ββεε-tetracarboxylate*, b.p. 210—216°/25 mm., hydrolysed (HCl) to *β*-methylpentane-*ββε*-tricarboxylic acid (**V**), m.p. 180° (lit. 141°) (*quinine* salt, $C_6H_{14}O_6{\cdot}2C_{20}H_{24}O_2N_2{\cdot}H_2O$, m.p. 199—201°, $[\alpha]_{5461}$ −160° in EtOH). The acid described by Roberts (A., 1926, 1125) as (**V**) is undoubtedly impure *γ*-hydroxy-*β*-methylpentane-*ββε*-tricarboxylic acid lactone (*loc. cit.*) [could not be reduced to (**V**)]. W. C. J. R.

Carboxylation of alkali salts of phenol.—See B., 1942, II, 185.

Indian lichens. IV. Constitution of montagnetol. V. S. Rao and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **15**, **A**, 18—23; cf. A., 1941, II, 265).—Montagnetol is shown to be erithrityl orsellinate. When pure, it has m.p. 156—157°, is $C_{12}H_{16}O_7$, gives the homofluorescein reaction slowly, with $CH_2Ac{\cdot}CO_2Et$ in H_2SO_4 at 0° gives 5-hydroxy-4 : 7-dimethylcoumarin, with boiling aq. $Ba(OH)_2$ or dil. H_2SO_4 (not cold) gives orcinol, CO_2, and erythritol (**I**), with cold conc. H_2SO_4 gives orsellinic acid and (**I**), with KOH–MeOH gives Me orsellinate (**II**), and with CH_2N_2 gives a viscous Me_2 ether and thence (KOH–MeOH) the Mc_2 ether of (**II**). R. S. C.

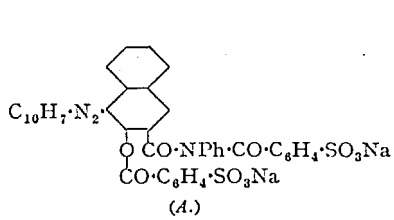
New class of atropisomeric compounds. A. Lüttringhaus and H. Gralheer (*Annalen*, 1941, **550**, 67—98).—A more detailed account of work previously reviewed (A., 1942, II, 9). A case of optical isomerism is described which depends on the inhibition of free rotation within the mol. This is due to the presence of a bridge ring which surrounds the rigid aromatic system like a handle. Such compounds are termed " ansa " substances and include ring systems which are condensed with aromatic nuclei in other than the usual *ortho-* or *peri*-positions. In certain cases resolvability is due to asymmetry of the whole mol. and depends on the outer ring being so narrow that revolution of the aromatic nucleus around the line of union is impossible. The theory is developed for a series of long-chained ethers of dihydric phenols and naphthols. Attempts to resolve racemic alcohols, their 3 : 5-dinitrobenzoates and keto-alcohols by fractional adsorption on *d*-tartaric acid, Ca *d*-tartrate, sucrose, or albumin were unsuccessful as were attempts to resolve 1 : 5-dihydroxynaphthalene $[CH_2]_{10}$ ether with *sec.*-butylpicramide. Gradual addition of 2·7N-KOH–EtOH to a boiling solution of 1 : 5-$C_{10}H_6(SH)_2$ and $Br{\cdot}[CH_2]_{10}{\cdot}Br$ in EtOH gives 5-*thiol*-1-*naphthyl κ-bromo*-n-*decyl sulphide*, transformed by very slow addition of its amyl alcoholic solution to K_2CO_3 in well-stirred amyl alcohol (apparatus described) into 1 : 5-*dithiolnaphthalene decamethylene ether*, m.p. 98—99°, into which ·CHO could not be introduced by Gattermann's method. 5 : 1-$OH{\cdot}C_{10}H_6{\cdot}O{\cdot}[CH_2]_{10}{\cdot}Br$ (A., 1937, II, 301) is converted by Br in CCl_4 into a *Br*-derivative, m.p. 54—55°, which further yields *bromo*-1 : 5-*dihydroxynaphthalene decamethylene ether*, b.p. 161—162°/0·05 mm., m.p. 56°, which could not be transformed into a Grignard compound by ordinary or Gilman Mg. *Toluquinol mono-κ-bromodecyl ether*, m.p. 42°, similarly yields the *decamethylene ether*, b.p. 106°/0·05 mm., into which suitable substituents could not be introduced. 2 : 5-*Dimethylquinol mono-κ-bromodecyl ether*, m.p. 62—63°, and *decamethylene ether*, m.p. 64°, 2-*bromo*-5-*methylquinol mono-κ-bromodecyl ether*, m.p. 64—65°, and *decamethylene ether*, b.p. 136—138°/0·08 mm., m.p. 61—62°, 2 : 5-*dibromoquinol mono-κ-bromodecyl ether*, m.p. 67°, and *decamethylene ether* (**I**), b.p. 167—168°/0·1 mm., m.p. 96°, 2 : 5-*dibromoquinol mono-μ-bromododecyl ether*, m.p. 71°, and *dodecamethylene ether*, two forms, m.p. 77—78° and 89°, are described. These cyclic ethers do not appear suitable for the introduction of substituents which would open the way to their resolution. Application of Wittig's method (A., 1939, II, 112) to (**I**), however, followed by treatment of the product with CH_2N_2 leads to *Me* 4-*bromogentisate decamethylene ether*, b.p. 166—167°/0·1 mm., hydrolysed to the r-*acid* (**II**), m.p. 114·5°. This is resolved by strychnine in abs. EtOH to (−)-4-*bromogentisic acid decamethylene ether* (**III**), m.p. 154°, $[\alpha]_D^{17}$ −37·2° in $COMe_2$ [*strychnine* salt (**IV**), m.p. 138—140°, $[\alpha]_D^{17}$ −58° in $CHCl_3$]. The acid obtained from the filtrates from (**IV**) gives (+)-4-*bromogentisic acid decamethylene ether* (**V**), m.p. 154°, $[\alpha]_D^{17}$ +37·5° in $COMe_2$, as the *cinchonine* salt, m.p. 205—209°, $[\alpha]_D^{17}$ +147·6° in $CHCl_3$. (**II**) is much less readily resolved by brucine (*salt*, $C_{40}H_{49}O_8N_2Br,H_2O,EtOH$, m.p. 103—105°, $[\alpha]_D^{17}$ −55° in $COMe_2$, described). Admixture of equal amounts of (**III**) and (**V**) gives (**II**), which is shown to be a normal mol. compound (1 : 1). The Na salt of (**V**) is optically stable in H_2O at 100° for 3 hr. and the Me ester of (**III**) is not racemised during hydrolysis by KOH–MeOH or when heated in PhMe at 210° for 4 hr. (**V**) is transformed by boiling 48% HBr–Ac_2O into $Br{\cdot}[CH_2]_{10}{\cdot}Br$ and 4-*bromogentisic acid*, m.p. 222° (decomp.). This is obtained synthetically by treatment of 2 : 5 : 1 : 4-$C_6H_2Br_2(OMe)_2$ with LiPh followed by CO_2 and then CH_2N_2, thus giving *Me* 4-*bromo*-2 : 5-*dimethoxybenzoate*, m.p. 96°, which is hydrolysed to the *acid*, m.p. 170°, and then treated with 48% HBr–Ac_2O. The stability of (**III**) and (**V**) confirms the views that aromatic nuclei exhibit a high degree of rigidity, the expenditure for their deformation exceeding the energy of activation of reactions which proceed with noticeable velocity between 100° and 200° and that the tetrahedral angle of the aliphatic C has an unexpectedly great straddling energy. 4-*Bromogentisic acid dodecamethylene ether*, m.p. 133—134°, in EtOH yields a *strychnine* salt, decomp. 175° (cloudy at 124°), $[\alpha]_D^{19}$ −52° in $CHCl_3$; the acid derived from this is optically inactive. It is impossible at present to decide whether the salt contains an active, very readily racemised acid or whether the acid is non-resolvable by reason of the too extensive bridge. H. W.

Structure and absorption of hydroxylic dyes derived from triphenylmethane. Tautomerism of the benzaurins and phthaleins.—See A., 1942, I, 194.

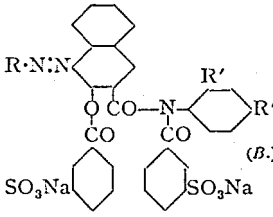
Coloured tautomeric forms in the benzaurin, phenolphthalein, and phenolsulphonephthalein series.—See A., 1942, I, 194.

Neocoton dyes, a new class of dye derivatives. C. Gränacher, H. Brüngger, and F. Ackermann (*Helv. Chim. Acta*, 1941, **24**, 40—71E).—Attempts are described to convert azo-dyes in general, and particularly those derived from 2 : 3-$OH{\cdot}C_{10}H_6{\cdot}CO{\cdot}NHAr$, into applicable, labile, sol. derivatives from which the initial dyé can easily be regenerated on the fibre. Treatment of 1-5′-chloro-2′-hydroxybenzeneazo-2-naphthol (**I**) with $ClSO_3H$ and dry C_5H_5N and of the product with Na_2CO_3 gives the Na salt of the sulphate. Only one OH can be thus affected and these types are unsuitable for the production of dyeings fast to washing in the sense of the ice colours. The prep. of *Na* 2-*hydroxy*-2′-*methoxy*-5 : 5′-*dimethylazobenzene sulphate* and *Na* 2-*hydroxy*-4′-o-*tolueneazo*-5 : 2′-*dimethylazobenzene sulphate*, as types, is described in detail. Esterification of such dye systems with $ClSO_3H$ is independent of mol. wt. and $C_{10}H_8$ or thiazole nuclei may be present. The essential condition is that the *o*-OH should be benzenoid. The ester salts are much lighter than the parent dyes. They are very stable towards alkalis but very sensitive to acids, which eliminate the acid residue and re-form the parent compound. Generally they cannot be prepared as dry, neutral specimens but are stable as alkaline pastes. The simplest ester salts are sufficiently sol. in H_2O but the solubility decreases rapidly with increasing mol. wt. so that a complete solution of the problem is not possible along these lines. 2-Hydroxy-1 : 1′-azonaphthalene (**II**) is transformed by *p*-$CH_2Cl{\cdot}C_6H_4{\cdot}COCl$ and C_5H_5N into 4″-*methylpyridinium chloride*-2′-*benzoyloxy*-1 : 1′-*azonaphthalene*, m.p. 244—245°, readily sol. in hot, sparingly sol. in cold H_2O. It is very readily hydrolysed by alkalis. Extension of the reaction leads to the following results. Treatment of (**II**) with *m*-$CO_2H{\cdot}C_6H_4{\cdot}SO_2Cl$ or *m*-$SO_3H{\cdot}C_6H_4{\cdot}COCl$ in C_5H_5N gives 2-benzoyloxy-1 : 1′-azonaphthalene-3″-sulphonic acid, isolated as the C_5H_5N and *Na* salts. The last named is readily hydrolysed but insufficiently sol. in H_2O. (**II**), C_5H_5N, and 1 : 3 : 5-$CO_2H{\cdot}C_6H_3(SO_2Cl)_2$ afford *Na* 2-*benzoyloxy*-1 : 1′-*azobenzene*-3″ : 5″-*disulphonate*, freely sol. in H_2O and readily hydrolysed. As examples of more complex dyes *Na*$_2$ 2-*methoxybenzene*-1-*azo*-1′-2′ : 5′-*dimethylbenzene*-4′-*azo*-1″-2″-*benzoyloxynaphthalene*-3‴ : 5‴-*disulphonate* and 2′-3′-sulphobenzoyloxynaphthalene-1-azo-1′-benzene-4′-azo-4″-2″-methoxy-5″-methylbenzene-1″-azo-1‴-2‴-(3⁗-sulphobenzoyloxy)naphthalene (as *Na*$_2$ salt) are cited. Since (**I**) is convertible into its 2 : 5′-di-*m*-sulphobenzoyl derivative (*Na*$_2$ salt) it follows that more replacement can be effected with acylating agents than with $ClSO_3H$ (see above). Treatment of azo-dyes from 2 : 3-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$ results in the entry of two acyl groups. Thus 1 : 2 : 3-$C_{10}H_7{\cdot}N_2{\cdot}C_{10}H_5(OH){\cdot}CO{\cdot}NHPh$ (**III**) gives the *dye* (*A*) which is freely sol. in H_2O and readily hydrolysed by alkali to the parent dye. Under the conditions employed it has never been found possible to introduce a single acyl into compounds of this type. With <2 mols. of BzCl (**III**) gives little or no 2(*O*) : 3(*N*)-

Bz_2 derivative, m.p. 170—171°. Further examples of compounds of this class are afforded by the *substances* (*B*) in which R = 2 : 5-$C_6H_3Cl_2$, R′ = OMe, and R″ = H; R = 4 : 2 : 5-



(*A.*)



(*B.*)

NHBz·C_6H_2(OEt)$_2$ and R′ = R″ = H; R = 4 : 2-C_6H_3ClMe, R′ = Me, and R″ = OMe. The H_2O-sol. products are termed "neocoton" dyes. They have the additional advantage that the individual members can be mixed in any desired proportion. Since 2-*ethoxy*-3-*naphtho*-N-*benzoylanilide*, m.p. 146—147°, is obtained from 2 : 3-OEt·$C_{10}H_6$·CO·NHPh and BzCl in C_5H_5N or from NHBzPh and 2 : 3-OEt·$C_{10}H_6$·COCl in boiling C_5H_5N, its constitution as an *N*-"diacyl" derivative is regarded as established and since acylation with SO_3H·C_6H_4·COCl proceeds similarly it is very probable that the dyes from 2 : 3-OH·$C_{10}H_6$·CO_2H are also *N*-"diacyl" compounds. The course of the hydrolysis of dibenzoylated derivatives of NH_2Ph depends greatly on the presence of substituents in the aniline and acyl residue. Thus, NBzPh·CO·C_6H_4·SO_3Na-*m* gives about 50% of the parent NHBzPh and 50% of SO_3H·C_6H_4·CO·NHPh, whereas *o*-C_6H_4Cl·NBz·CO·C_6H_4·SO_3Na-*m* gives ~71% of *o*-C_6H_4Cl·NHBz, whilst only ~35% of *o*-C_6H_4Cl·NH·CO·C_6H_4·NO_2-*p* is regenerated from *p*-NO_2·C_6H_4·CO·N(C_6H_4Cl-*o*)·CO·C_6H_4·SO_3Na-*m*. 2 : 3-OEt·$C_{10}H_6$·CO·NPh·CO·C_6H_4·SO_3Na-*m* gives >99% of the initial anilide. 2 : 3-OEt·$C_{10}H_6$·COCl and NHBzPh in C_5H_5N very readily afford *di*-(2-*ethoxy*-3-*naphth*)*anilide*, m.p. 233—234°.

H. W.

Sulphocarboxylic acids. II. 3-Nitro-5-sulphobenzoyl chloride and its application to the synthesis of polyamides. P. Ruggli and F. Grün (*Helv. Chim. Acta*, 1941, **24**, 9—23E; cf. A., 1941, II, 225).—3 : 5 : 1-NO_2·C_6H_3(SO_3H)·CO_2H (**I**) (prep. from BzOH and purification through the Ba H_2 salt described) gives a *Ba* salt, [NO_2·C_6H_3(CO_2H)·SO_3]$_2$Ba + 2[NO_2·C_6H_3(CO_2)·SO_3]Ba, anhyd. and +10H_2O, a normal *Sr* salt (+4H_2O), and a *NH*$_3$*Ph H* salt, m.p. 235° (decomp.). (**I**) is resistant towards $SOCl_2$ alone or in presence of $AlCl_3$ or of an inert solvent at 120° but in presence of small amounts of *m*-SO_3H·C_6H_4·CO_2H, AcOH, or preferably I, is converted into 3-*nitro*-5-*sulphobenzoyl chloride* (**II**) with a small proportion of an amorphous polyanhydride which gives the same products as (**II**) with amines. 3 : 5 : 1-NO_2·C_6H_3(SO_2Cl)·COCl and NH_2Ph in Et_2O afford the corresponding *dianilide*, m.p. 188°, whilst 3 : 5 : 1-NO_2·C_6H_3(SO_2Cl)·CO_2H (**III**) yields the *anilide*, m.p. 177°. (**II**) and NH_2Ph in boiling Et_2O yield 3 : 5 : 1-NO_2·C_6H_3(SO_2H)·CO·NHPh, isolated as *NH*$_2$*Ph* salt (**IV**), m.p. 260° (decomp.), K, Na, Pb, or *Ba* (+6H_2O) salts. 3 : 5 : 1-NO_2·C_6H_3(SO_3H)·CO·NH_2 is isolated as the *NH*$_4$ salt. (**III**) and dry C_5H_5N at 70° give an additive product transformed by NH_2Ph in boiling Et_2O into (**IV**); 3 : 5 : 1-NO_2·C_6H_3(SO_2·NHPh)·CO·NHPh or 3 : 5 : 1-NO_2·C_6H_3(SO_2·NHPh)·CO_2H is not formed. 3 : 5 : 1-NH_2·C_6H_3(SO_3H)·CO_2H (**V**) in dry C_5H_5N reacts smoothly with BzCl in dioxan at 0°, then at room temp., and finally at 70° to give 3 : 5 : 1-NHBz·C_6H_3(SO_3H)·CO_2H, isolated as the *Sr H*$_2$ salt (+8H_2O). Under these conditions the analogous reaction with *m*-NO_2·C_6H_4·COCl is much less complete but with an excess and dioxan–Sr(OH)$_2$ 3 : 5 : 1-*m*-NO_2·C_6H_4·CO·NH·C_6H_3(SO_3H)·CO_2H is formed in good yield and is isolated as the *Sr* (+6H_2O) (**VI**) and *Sr H*$_2$ (+6H_2O) salts. (**VI**) is reduced by $FeSO_4$ and Sr(OH)$_2$ to 3-m′-*aminobenzamido*-5-*sulphobenzoic acid* (+3H_2O), m.p. (anhyd.) >350° (decomp.). (**II**) and (**V**) in abs. dioxan kept faintly alkaline by addition of powdered Sr(OH)$_2$ at 60° give 3-3′-nitro-5′-sulphobenzamido-5-sulphobenzoic acid, m.p. ~270° [*Sr* salt (+22H_2O)], which is freely sol. in H_2O. The Sr salt is reduced [$FeSO_4$ + Sr(OH)$_2$] to 3-3′-amino-5′-sulphobenzamido-5-sulphobenzoic acid isolated as the *Sr* (+22H_2O) and *Sr H*$_2$ (+4H_2O) salts. The former salt and (**II**) analogously afford 3-3′-3″-nitro-5″-sulphobenzamido-5′-sulphobenzamido-5-sulphobenzoic acid [*Sr*$_2$ salt (+12H_2O)].

H. W.

Dicyanostilbenes.—See B., 1942, II, 186.

Aldehyde–cyanohydrin reaction. Mesomeric effect of alkyl groups.—See A., 1942, I, 204.

Condensation of aldehydes with amides. IX. Condensation of *o*-nitrobenzaldehyde. P. I. Ittyerah and K. C. Pandya (*Proc. Indian Acad. Sci.*, 1942, **15**, **A**, 6—10; cf. A., 1942, II, 16).—*o*-NO_2·C_6H_4·CHO and RCO·NH_2, when heated alone or in presence of a trace of C_5H_5N, give *o*-NO_2·C_6H_4·CH(NH·COR)$_2$ (usually ~50%). Thus are obtained *o*-nitrobenzylidenebis-formamide, m.p. 177°, -acetamide, m.p. 235° (lit. 231—232°), -*propionamide*, m.p. 223—225°, -n-*butyramide*, m.p. 181°, -n-*heptoamide* (97·1%), m.p. 135°, -benzamide, m.p. 251—252° (lit. 217—218°), and -*phenylacetamide*, m.p. 229—230°.

R. S. C.

Friedel–Crafts reaction. VII. Action of phthalic and succinic anhydrides on resorcinol derivatives. R. D. Desai and F. Figueredo (*Proc. Indian Acad. Sci.*, 1941, **14**, **A**, 605—608).—*m*-C_6H_4(OH)$_2$, *o*-C_6H_4(CO)$_2$O, and $AlCl_3$ in PhNO_2, first at room temp. and then at 100° (bath), give o-2′ : 4′-*dihydroxybenzoylbenzoic acid*, m.p. 202° (Br_1-derivative, m.p. 220°), reduced (Clemmensen) to o-2′ : 4′-*dihydroxybenzylbenzoic acid*, m.p. 143°. *m*-C_6H_4(OMe)$_2$ and -OH·C_6H_4·OMe similarly give the same o-2′-*hydroxy*-4′-*methoxybenzoylbenzoic acid*, m.p. 165° (Br_1-derivative, m.p. 203°). β-2 : 4-Dihydroxybenzoylpropionic acid [reduced (Clemmensen) to γ-2 : 4-*dihydroxyphenylbutyric acid*, m.p. 105°] gives a Br_1-derivative, m.p. 190°, which with Me_2SO_4 and 10% NaOH affords 5-*bromo*-β-2-*hydroxy*-4-*methoxybenzoylpropionic acid* (**I**), m.p. 203°, further methylated (Me_2SO_4, K_2CO_3, $COMe_2$) to β-5-*bromo*-2 : 4-*dimethoxybenzoylpropionic acid* (**II**), m.p. 179°. (**I**) and (**II**) are also obtained by brominating the corresponding acids.

W. C. J. R.

***meso*Benzanthronecarboxylic acids.** F. C. Copp and J. L. Simonsen (*J.C.S.*, 1942, 209—213).—Diphenylmethane-2 : 4′-dicarboxylic acid (convenient prep. described), glycerol (**I**), and 90% H_2SO_4 at 100—120° give *meso*benzanthrone-9-carboxylic acid (**II**), m.p. 352—354° (*Me*, m.p. 188—189°, and *Et*, m.p. 172·5—173·5°, ester), the structure of which is proved by its conversion (NaN_3, H_2SO_4–$CHCl_3$) into 9-*amino*mesobenzanthrone, m.p. 216—217° (*Ac* derivative, m.p. 252—254°; gives 9-chloro*meso*benzanthrone), and by its formation by oxidation (SeO_2, H_2O, 230—240°) of 9-methyl-*meso*benzanthrone. Anthraquinone-2-carboxylic acid, (**I**), 90% H_2SO_4, and a trace of Zn dust at 110—120° yield (**II**) and a little mesobenzanthrone-10-*carboxylic acid* (**III**), m.p. 326—327° (*Me*, m.p. 167—168°, and *Et*, m.p. 136—138° after softening at 134°, ester); (**II**) and (**III**) are separated chromatographically as the Et esters. *meso*Benzanthrone-4-carboxylic acid, m.p. 314—315° (*Me*, m.p. 215—216°, and *Et*, m.p. 134—135°, ester), is prepared by oxidation (PhNO_2, KOH, 140—150°) of 4-methyl*meso*benzanthrone; the 10-Me derivative is best oxidised to (**III**) by SeO_2 in PhNO_2. Anthraquinone-1-carboxylamide, (**I**), NH_2Ph, and Cu-bronze in 90% H_2SO_4 at 95—100° yield mesobenzanthrone-8-*carboxylic acid* (**IV**), m.p. 254—255° (*Me* ester, m.p. 173·5—174·5°), and (mainly) *meso*benzanthrone-11-carboxylamide; (**IV**) is oxidised (CrO_3, AcOH) to anthraquinone-1 : 5-dicarboxylic acid. Anthraquinone-1-carboxylic acid or its anthrone does not condense with (**I**) probably owing to lactonisation.

W. C. J. R.

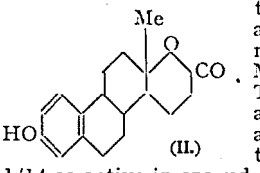
Identity of the red pigment in roots of *Tripterygium wilfordii* and *Celastrus scandens*.—See A., 1942, III, 426.

IV.—STEROLS AND STEROID SAPOGENINS.

Steroids. XXXII. Constitution of cafesterol. A. Wettstein, H. Fritzsche, F. Hunziker, and K. Miescher (*Helv. Chim. Acta*, 1941, **24**, 332—358E).—Fractional crystallisation of (crude) cafesteryl acetate (**I**) from MeOH or hexane, chromatography (Al_2O_3), or conversion into its *adduct* (**II**) with (CH·CO)$_2$O, m.p. 187—189° (decomp.), $[\alpha]_D^{17}$ −35°±2° in $CHCl_3$, leads to a homogeneous acetate, m.p. 169—171° (decomp.), $[\alpha]_D^{18}$ −100°±2° in $CHCl_3$, hydrolysed to cafesterol (**III**), m.p. 160—162° (sinters at 158°), $[\alpha]_D^{20}$ −107°±2° in $CHCl_3$. (**III**) is sensitive to light and acid whereas (**I**) is considerably more stable. (**I**) is devoid of œstrogenic action. Analyses of (**III**) and its derivatives agree with the formula $C_{20}H_{28}O_3$. (**I**) has one active H, does not react with carbonyl reagents, and does not contain OAlk. The existence of (**II**) establishes the presence of conjugated double linkings and their presence in one and the same ring is in harmony with the absorption spectrum and other properties. There is no indication of the presence of an αβ-unsaturated ketone. (**III**) is transformed by Pb(OAc)$_4$ into CH_2O and *oxnorcafestadienone* (**IV**), $C_{19}H_{24}O_2$, m.p. 176—178°, $[\alpha]_D^{17}$ −99°±2° in $CHCl_3$ [*monosemicarbazone*, m.p. 245—246° (decomp.); *adduct* with (CH·CO)$_2$O, m.p. 190° (decomp.)], which does not reduce Ag solution or give a colour with $FeCl_3$. (The fundamental saturated hydrocarbon is termed "cafestane" and "ox" indicates O present in a masked CO or ether group.) The newly-formed CO is not in conjunction with the double linkings. (**IV**) is reduced by Al(OPr$^\beta$)$_3$ to *oxnorcafestadienol* (**V**), $C_{19}H_{26}O_2$, characterised as the *acetate*, m.p. 165—167·5°. (**IV**) and (**V**) retain the system of double linkings and the inert O of (**III**). In general, hydrogenation of (**III**) leads to a complex mixture of isomerides but treatment of (**I**) in EtOH containing Pd–C gives a good yield of homogeneous *tetrahydrocafesteryl* [*oxcafestanediol*] *monoacetate*, m.p. 153—154°, which contains only one active H, does not give a semicarbazone, and is unchanged by Ac_2O–C_5H_5N at room temp., thus showing that only the C:C double linkings have been hydrogenated. Since it is saturated, the presence of only two double linkings in (**III**) is established. It is hydrolysed (aq. MeOH–K_2CO_3) to *oxcafestanediol*, $C_{20}H_{32}O_3$, m.p. 160—163°, which is oxidised by HIO_4 to *oxnorcafestanone* A (**VI**), m.p. 133—134·5°, in which >C(OH)·CH_2·OH has been replaced by CO. (**VI**) is saturated, does not reduce Ag solution, does not contain an active H, and affords a *monosemicarbazone*, m.p. 219—221°. The new CO is active whereas the second O remains inert. (**VI**) has no androgenic action. It is isomeric with androstane-3 : 17-dione

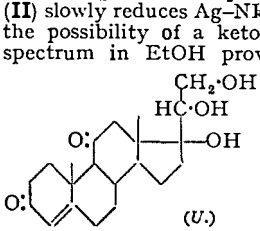
and ætiocholane-3 : 17-dione, with which it gives marked depression of m.p. When energetically reduced with Zn–Hg and HCl it gives non-cryst. products. Oxidation of (**VI**) with aq. MeOH–KOI gives small amounts of a neutral substance and, mainly, a dicarboxylic *acid* (**VII**), $C_{19}H_{28}O_5$, m.p. 224—227° (decomp.), the formation of which can only be explained by fission between cyclic CO and vicinal CH_2. That this CO is identical with that formed by degradation of the side-chain and not with the inert O is proved by the inability of the Me_2 ester, m.p. 78·5—80°, of (**VII**) to give a semicarbazone. (**III**) therefore contains the group $\cdot CH_2 \cdot C(OH) \cdot CH_2 \cdot OH$. Since (**VII**) is very readily (Ac_2O–C_5H_5N at room temp.) converted into an *anhydride*, m.p. 204—206°, which does not pass into a ketone when heated above its m.p. it is probable that this arrangement is part of a 5-membered ring. *t*-Dehydroandrosterone acetate behaves analogously when oxidised with Ol'. The acid fraction, after acetylation, gives Δ^5-3*t*-acetoxyætiobilienic anhydride, m.p. 190·5—191·5°, whilst the neutral portion contains Me_2 Δ^5-3*t*-acetoxyætiobilienate, m.p. 156—157°. Clemmensen reduction of (**VII**) does not lead to a homogeneous product and milder treatment leaves it untouched. Hydrogenation (PtO_2 in AcOH) of (**I**) ultimately involves the fixation of 3 H_2, giving a mixture (**VIII**) from which a *cafestanetriol monoacetate*, m.p. 189—190°, is isolated (similar treatment of the corresponding H_4-compound gives less definite results). Hydrolysis of (**VIII**) followed by oxidation by HIO_4 gives (**VI**) but mainly *oxnorcafestanone* B (**IX**), m.p. 167—168·5°. (**IX**) is saturated, does not contain an active H, and yields a *semicarbazone*, m.p. 257—259° (decomp.). (**VI**) and (**IX**) are accompanied by *norcafestanolone* A (**X**), m.p. 180—181°, which is non-reducing, gives a *monosemicarbazone*, m.p. 225° (decomp.), and an *acetate*, m.p. 200—201°, but does not form a sparingly sol. compound with digitonin. The *sec.* nature of OH in (**X**) is shown by oxidation to *norcafestanedione*, m.p. 141—142°. This is saturated and non-reducing, does not contain an active H, and gives a *disemicarbazone* (**XI**), m.p. 378° (decomp.). It is isomeric with androstane-3 : 17-dione and ætiocholane-3 : 17-dione, with which it gives very marked depression of the m.p. It is not androgenic. (**XI**) is reduced (Wolff–Kishner) to *norcafestane*, $C_{19}H_{32}$, m.p. 81·5—83°, $[\alpha]_D^{20}$ −48° in hexane. Under similar conditions androstanedionedisemicarbazone is reduced to androstane. M.p. are corr. H. W.

Oxidation of œstrone by hydrogen peroxide. W. W. Westerfeld (*J. Biol. Chem.*, 1942, **143**, 177—184; cf. A., 1940, III, 652).—The phenolic ring of œstrone (**I**) is not attacked by 10% H_2O_2–aq. NaOH at room temp.; a OH-acid is formed, readily losing H_2O to give the *lactone* (**II**), m.p. 335—340° (softens and turns brown at 330°) [*monoacetate*, m.p. 143·5—145°; *Me ether* (prep. by Me_2SO_4–aq. NaOH), m.p. 166—168°]. The absorption spectra of (**II**) and its acetate are similar to those of (**I**) and its acetate. (**II**) gives a negative reaction in the Kober and Zimmermann tests and is 1/14 as active in spayed mice as is (**I**). (**II**) and MeOH–HCl yield a mixture of *esters* in which the lactone ring is opened; MeOH–H_2SO_4 also give a mixture, in which the CO_2H is completely methylated and 50% of the ester is dehydrated by loss of *tert.* OH. *cyclo*-Pentanone and H_2O_2–aq. NaOH at 35—40° give δ-valerolactone; the derived δ-hydroxyvaleric acid (*Ag* salt) is oxidised ($KMnO_4$) to glutaric acid. A. T. P.



(II.)

Constituents of the adrenal cortex and related substances. LIV. Methods of separation; isolation of substance *U* and its partial synthesis from substance *E*. T. Reichstein and J. von Euw (*Helv. Chim. Acta*, 1941, **24**, 247—264E).—Chromatographic separation after acetylation has been extended with good results to the $C_{21}O_5$ group although frequently a considerable expenditure of material is necessitated by the close relationship of the compounds. Preseparation and concn. of the extracts are considerably facilitated by the use of pure EtOAc and of $KHCO_3$ in aq. MeOH at room temp. for the hydrolysis of any esters which may be present. Distribution of the main keto-fraction of the concentrates of the adrenal cortex hormones (separated by Girard's reagent) between C_6H_6 and H_2O gives substance *E* in the portions most freely sol. in H_2O. This is characterised by a well-cryst. *diacetate* (**I**), m.p. 229—230°, $[\alpha]_D^{22}$ +162·7°±2° in $COMe_2$. The residues from *E* when acetylated and chromatographed give more (**I**) and, in addition, relatively considerable quantities of *substance* U *diacetate* (**II**), m.p. 252—253°, $[\alpha]_D^{21}$ +178·5°±2° in $COMe_2$; it is hydrolysed to *substance* U, m.p. 208°. (**II**) slowly reduces Ag–NH_3 solutions at room temp., thus excluding the possibility of a ketol side-chain. Its ultra-violet absorption spectrum in EtOH proves it to be an αβ-unsaturated ketone. Cautious oxidation of (**I**) with CrO_3 gives (**II**), thus establishing the constitution of *U* and proving that *U* and *E* have the same configuration at $C_{(17)}$ and $C_{(20)}$. Complete hydrogenation (PtO_2 in AcOH) of (**II**) and acetylation of the product leads to substance *A* triacetate (**III**) in 23% yield. Hence *A*, *E*, and *U* have the same configuration at $C_{(17)}$ and $C_{(20)}$ and OH at $C_{(11)}$ is similarly orientated in *A* and *E*. In this hydrogenation >2 H are absorbed indicating a partial removal of O, which is confirmed by the isolation of an (impure) by-product with an O content < that of (**III**). M.p. are corr. H. W.



(*U*.)

Steroids and sex hormones. LXXHI. *D*-Homoœstrone and *D*-homocestradiol. M. W. Goldberg and S. Studer (*Helv. Chim. Acta*, 1941, **24**, 295—302E).—The mixture of epimeric œstronecyanohydrin 3-monoacetates (A., 1941, II, 257) is separated by fractional crystallisation from EtOAc–hexane into its *components* (**I**), m.p. 151—153° (decomp.), $[\alpha]_D^{24}$ +27·6°±2° in dioxan [diacetate (**II**), new m.p. 232—233°, $[\alpha]_D^{24}$ +25·5°±2° in dioxan] (main portion), and (**III**), m.p. 170—171°, $[\alpha]_D^{20}$ +15·40°±2° in dioxan [*diacetate*, m.p. 233—235°, $[\alpha]_D^{20}$ +11·6°±2° in dioxan, which does not depress the m.p. of (**II**)]. (**I**) is reduced (H_2–PtO_2–AcOH) to 17-aminomethylœstradiol 3-monoacetate, analysed as the very hygroscopic *picrate*, m.p. 233—234° (decomp.). *D*-Homoœstrone (**IV**) (*loc. cit.*) is hydrogenated (PtO_2 in 2·5% KOH–MeOH) to *D-homoœstradiol*, m.p. 232·5—233°, $[\alpha]_D^{24}$ +87·6°±2° in dioxan [*diacetate*, m.p. 165—165·5° (vac.)], with, apparently, an isomeric diol; it has about the same physiological activity as (**IV**). Me_2SO_4, (**IV**), and 10% KOH yield *D-homoœstrone Me ether*, m.p. 138·5—139·5° (vac.), $[\alpha]_D^{21}$ +31°±2° in dioxan, transformed by Na and *iso*amyl formate in abs. Et_2O into 17-*hydroxymethylene*-*D*-*homoœstrone Me ether*, m.p. 195—197° (vac.). M.p. are corr. H. W.

Transformation of scillaren-*A* into *epiallo*lithocholic acid.—See A., 1942, II, 81.

V:—TERPENES AND TRITERPENOID SAPOGENINS.

Substances with odour of violets. X. Merling and Welde's alleged irone synthesis. L. Ruzicka and W. Brugger (*J. pr. Chem.*, 1941, [ii], **158**, 125—129).—The irone synthesis (Tiemann and Kruger's structure) of Merling and Welde (A., 1909, i, 479) is adversely criticised. A repetition of their work shows that their supposed Δ^4-*cyclo*geranic acid is, in reality, the Δ^2-isomeride, α-*cyclo*geranic acid. The identity is established by mixed m.p. with the acids, their anilides and *p*-toluidides, by the identical stabilities of their dibromides, and, finally, by the ozonolysis of both acids to *iso*geronic acid (semicarbazone, m.p. 197—198°) in identical yield. It follows that Merling and Welde's synthetic irone was, in reality, α-ionone. Verley's synthesis of "irone" (A., 1935, 979) could not be repeated. H. N. R.

Constitution and colour of azulene.—See A., 1942, II, 191.

Terpin esters.—See B., 1942, II, 97.

Terpene cyanoacetyl compounds.—See B., 1942, II, 145.

Influence of the method of reduction on the formation of stereoisomerides. Catalytic reduction of 2 : 3-camphorquinone. H. Rupe and F. Müller (*Helv. Chim. Acta*, 1941, **24**, 265—282E).—Catalytic reduction of 2 : 3-camphorquinone (**I**) gives results quite different from those of the older methods of reduction particularly with reference to the different stereoisomerides. (**I**) is quantitatively reduced in presence of a Ni catalyst, readily at room pressure, much more readily under increased pressure, to a *dihydroxycamphane* (*glycol* II) (**II**), m.p. 253—255° (in sealed capillary), $[\alpha]_c^{20}$ −11·68°, $[\alpha]_{Cn}^{20}$ −12·84°, $[\alpha]_D^{20}$ −14·60°, $[\alpha]_{Hg}^{20}$ −17·03°, $[\alpha]_{Cu}^{20}$ −19·47°, $[\alpha]_F^{20}$ −21·90° in EtOH. It differs entirely from the dihydroxycamphane (now called "glycol I") (**III**) obtained by Manasse by reduction of (**I**) with Zn dust and AcOH. The rotatory dispersion curve indicates the possibility that (**II**) is not completely homogeneous. It is characterised by a cyclic *sulphite*, m.p. 55°, an *iso*-*propylidene* compound, b.p. 109—110°/11 mm., $[\alpha]_D^{20}$ −9·31°, an *acetate*, b.p. 142°/12 mm., and a *benzoate*, m.p. 108—110°, thus indicating that it is a *cis*-compound. (**III**) is probably a *trans*-derivative which is possibly not completely homogeneous. With $SOCl_2$ it affords a small amount of a white compound which has not been investigated but it does not yield a $:CMe_2$ derivative. (**II**) and (**III**) behave similarly towards $Pb(OAc)_4$. (**II**) gives ill-defined results when treated with HBr in AcOH, PCl_5, PCl_3, or PBr_3. It is not attacked by Me_2SO_4, CH_2N_2, MeI, or MeOH–HCl. It is oxidised by $KMnO_4$ in alkaline solution to *cis-d*-camphoric acid, m.p. 183—184°. Partial hydrogenation (Ni–aq. EtOH) of (**I**) gives α-*hydroxycamphor* (**IV**), m.p. 210—211°, $[\alpha]_D^{20}$ +115·58° in C_6H_6 [purified through the *semicarbazone* (**V**), m.p. 199—201°, $[\alpha]_D^{20}$ −8·24° in EtOH], which is reduced by Na–Hg in warm H_2O to camphor, m.p. 174—176°, transformed by Br at 100° into α-bromocamphor, m.p. 74—75° (**VI**). Further hydrogenation (Ni) of (**IV**) gives (**II**) whereas treatment with Na in boiling EtOH leads to a compound regarded as the pure form of (**III**), m.p. 227—229°, $[\alpha]_D^{20}$ +17·76° in EtOH. The mother-liquors from (**V**) contain (**II**) and the *semicarbazone*, m.p. 196—198°, of a second new α-*hydroxycamphor* (**VII**), m.p. 210—213°, $[\alpha]_D^{20}$ +9·81° in EtOH. (**VII**) is converted by successive reduction and bromination into (**VI**) and is hydrogenated (Ni) to (**II**). (**I**) is reduced (Manasse–Bredt) to a mixture of α- (**VIII**) and β- (**IX**) -hydroxycamphor. (**VIII**) and (**IX**) are hydrogenated (Ni) as their mixture or separately to another *dihydroxycamphane* (*glycol*

III), m.p. 227—228°, $[\alpha]_D^{20}$ +26·7° in EtOH (*sulphite*, m.p. 57—59°). Reduction of (**VIII**) or (**IX**) by Na and boiling EtOH yields a glycol, m.p. 230—231°, $[\alpha]_D^{20}$ +17·6° in EtOH. H. W.

Camphorylidenesulphanilamides.—See B., 1942, III, 114.

Camphenilone, camphene hydrate, and methylcamphenilol. W. Hückel [with W. Doll, S. Eskola, H. Weidnecr, and, in part, F. Neumann and I. Schneider] (*Annalen*, 1941, **549**, 186—208).—The following data are recorded for optically homogeneous substances: camphene, $[\alpha]_D^{20}$ +107·7° in C_6H_6, +99·6° in EtOH (vals. for other solvents and λ also recorded); ω-nitrocamphene (from light petroleum), m.p. 85°, $[\alpha]_D^{21\cdot8}$ +153·4° in C_6H_6, $[\alpha]_D^{23\cdot5}$ +184·4° in EtOH (from MeOH), m.p. 85—86°, $[\alpha]_D$ +149·6° in C_6H_6, +176·0° in EtOH; camphenilone, b.p. 78°/12 mm., 193°/761 mm., m.p. 38—39°, $[\alpha]_D^{23\cdot5}$ +66·7° in C_6H_6, $[\alpha]_D$ +70·4° in EtOH (hydrazone, b.p. 103—103·5°/8 mm., m.p. 27—28°, $[\alpha]_D^{20}$ +223·4° in EtOH; azine, m.p. 142—143°, $[\alpha]_D^{20}$ +304° in C_6H_6; semicarbazone, m.p. 223°, $[\alpha]_D^{17}$ +263° in $CHCl_3$; *oxime* (possibly two compounds), m.p. 115—118°, $[\alpha]_D^{18}$ +173° in C_6H_6, and m.p. 123°, $[\alpha]_D^{20}$ +160° in C_6H_6); fenchone, m.p. +5·5°, $[\alpha]_D^{20}$ +66·9°, $[\alpha]_D^{16}$ +69·8° in EtOH, +65·9° in C_6H_6; camphenilane, b.p. 142·5°/753 mm., m.p. 17·5°, $[\alpha]_D$ −10·76°, $[\alpha]_D^{20}$ −11·2° in EtOH, −12·3° in C_6H_6; camphenilol II, m.p. 75—76°, $[\alpha]_D^{21}$ +23·59° in EtOH, $[\alpha]_D^{22}$ +23·39° in *cyclo*hexane (*p-toluenesulphonate*, m.p. 69—70°, decomp. ~165°, $[\alpha]_D^{20}$ +21·5° in *cyclo*hexane; 3 : 5-*dinitrobenzoate*, m.p. 145—145·5°, $[\alpha]_D^{20}$ +31·4° in C_6H_6); methylcamphenilol (*p-nitrobenzoate*, m.p. 134—135°, $[\alpha]_D^{17}$ +40·3° in C_6H_6, best obtained by action of BzCl on the K derivative of the alcohol in light petroleum; the *p-nitrobenzoate* of inactive methylcamphenilol has m.p. 153°); camphene hydrate (*p-nitrobenzoate*, m.p. 96°, $[\alpha]_D$ −24·9° in EtOH, −32·6° in C_6H_6; *p-benzamidobenzoate*, m.p. 129°, $[\alpha]_D^{20}$ −12·8° in C_6H_6; 3 : 5-*dinitrobenzoate*, m.p. 112°, $[\alpha]_D^{17}$ −24·9° in abs. EtOH); camphene hydrochloride, m.p. 124—125°, $[\alpha]_D$ −42·0° in C_6H_6; *l*-bornyl 3 : 5-dinitrobenzoate, m.p. 156—157°, $[\alpha]_D^{18}$ −25·2° in C_6H_6; *d*-bornyl *p*-nitrobenzoate, m.p. 136—137°, $[\alpha]_D^{20}$ +21·9° in C_6H_6; *dl-iso*bornyl *p*-nitrobenzoate, m.p. 131—132°; *l-iso*bornyl *p*-nitrobenzoate, m.p. 120°, $[\alpha]_D$ −54·2° in C_6H_6; *l-iso*bornyl 3 : 5-dinitrobenzoate, m.p. 139—140° $[\alpha]_D^{18}$ −44·8° in C_6H_6; *dl-iso*bornyl 3 : 5-dinitrobenzoate, m.p. 132—133°; *iso*camphanol II, m.p. 64°, $[\alpha]_D^{24}$ +8·43° in EtOH, $[\alpha]_D^{20\cdot5}$ +8·36° in C_6H_6 [3 : 5-dinitrobenzoate, m.p. 109·5° (with possibly a form, m.p. 79°), $[\alpha]_D^{20}$ +11·78° in C_6H_6]; *iso*camphanol I, m.p. 68·5—70° $[\alpha]_D^{21}$ −5·44° in EtOH, −5·68° in C_6H_6 (3 : 5-*dinitrobenzoate*, m.p. 99—101°, $[\alpha]_D^{19\cdot5}$ −11·50° in C_6H_6; camphenilanaldehyde, b.p. 94—95·5°/13 mm., $[\alpha]_D^{23}$ +90·6° in EtOH, +93·1° in C_6H_6, and its enol acetate, b.p. 108—109°/13 mm., $[\alpha]_D$ −25·9°. H. W.

Triterpene group. IX. Constitution of brein and maniladiol. (Miss) I. M. Morice and J. C. E. Simpson (*J.C.S.*, 1942, 198—203).—A close structural relationship probably obtains between brein (**I**) and maniladiol (**II**), both being singly unsaturated, pentacyclic, disecondary glycols, differing in the location of the ethenoid linkings but possibly with identical OH positions. There is no close association either between the OH groups themselves, or between these and the double linking, in either diol. Oxidation (CrO_3) of the diacetate of (**I**) gives *breienediolone diacetate*, m.p. 222—223°, $[\alpha]_D^{17}$ +90°, hydrolysed (KOH) to breienediolone, m.p. 247—249° (efferv.), $[\alpha]_D^{21}$ +82°. Oxidation (CrO_3) of (**I**) yields breienedione, m.p. 150—151°, $[\alpha]_D^{16}$ +67°, or 159—160°, $[\alpha]_D^{17}$ +66°, which although forming a monoxime, m.p. 250—252° (decomp.), is reduced (Clemmensen) to a *hydrocarbon*, $C_{30}H_{48}$, m.p. 142—143°, $[\alpha]_D^{13}$ +40°, and by $Al(OPr^{\beta})_3$ to a mixture of *breieneonol*-A (**III**), m.p. 208—209°, $[\alpha]_D^{17}$ +37° (*acetate*, m.p. 133—135°, $[\alpha]_D^{22}$ −13°) and -B, m.p. 226—227°, $[\alpha]_D^{18}$ +48° (*acetate*, m.p. 212—213°, $[\alpha]_D^{23}$ +46°). Attempts to methylate (**I**) and (**III**) have been unsuccessful. α-Amyrin is methylated to the *Me ether*, m.p. 221—222°, $[\alpha]_D^{15}$ +93°, and β-*amyrin Me ether* has m.p. 247—248°, $[\alpha]_D^{10}$ +98°. β-*Amyrin* *p-toluenesulphonate*, m.p. 132—138° (decomp.), is described. Oxidation (CrO_3) of (**II**) gives *maniladione*, m.p. 209—210°, $[\alpha]_D^{17}$ +48° [*monoxime*, m.p. 272—274° (decomp.)], which is further oxidised (CrO_3) to an *acid*, $C_{30}H_{46}O_5$, m.p. 270—272° (decomp.), and a neutral *substance*, $C_{30}H_{44}O_3$, m.p. 227—229·5°, $[\alpha]_D^{15}$ +155°. The diketone is reduced (N_2H_4–NaOEt) to a *substance*, $C_{30}H_{50}O$, m.p. 177—179°, $[\alpha]_D^{22}$ +50°. Oxidation (CrO_3) of the diacetate of (**II**) affords the *keto-acetate*, m.p. 224—225°, $[\alpha]_D^{16}$ +93°, hydrolysed (KOH) to the *keto-diol*, m.p. 240—241° (efferv.), $[\alpha]_D^{21}$ +88°. All rotations are in $CHCl_3$. F. R. S.

Dehydroabietic acid derivatives.—See B., 1942, II, 186.

VI.—HETEROCYCLIC.

Benzfurans.—See B., 1942, II, 172.

Heterocyclic compounds. XV. Coumarins from pyrogallol derivatives. XVI. Coumarins from quinol derivatives. R. D. Desai and C. K. Mavani (*Proc. Indian Acad. Sci.*, 1942, **15, A**, 1—5, 11—15; cf. A., 1942, II, 108).—XV. 1 : 2 : 3-$C_6H_3(OH)_3$ (**I**), $NaHCO_3$, and Na_2SO_4 in H_2O give 50% of 2 : 3 : 4 : 1-$(OH)_3C_6H_2{\cdot}CO_2H$ (**II**). 2 : 3 : 4 : 1-$(OH)_3C_6H_2{\cdot}CO_2R$ with $CHRAc{\cdot}CO_2Et$ in 73% H_2SO_4 gives 7 : 8-*dihydroxy*-6-*carbomethoxy*-4-*methyl*- (30%), m.p. 209°, -6-*carbethoxy*-4-*methyl*- (25%), m.p. 211°, -6-*carbethoxy*-3 : 4-*dimethyl*- (10%), m.p. 230°, -6-*carbethoxy*-4-*methyl*-3-*ethyl*- (8%), m.p. 209—210°, and -6-*carbomethoxy*-4-*methyl*-3-n-*propyl*- (6—8%), m.p. 203—204°, -*coumarin* and with $CH_2Bz{\cdot}CO_2Et$ gives 7 : 8-*dihydroxy*-6-*carbethoxy*-4-*phenylcoumarin* (6%), m.p. 217°. 3 : 4 : 5 : 1-$(OH)_3C_6H_2{\cdot}CO_2R$ (R = H, Me, or Et) and (**II**) do not undergo this condensation. 1 : 2 : 3 : 4-$C_6H_2Ac(OH)_3$, best (65—70%) obtained from 1 : 2 : 3-$C_6H_3(OAc)_3$ by $AlCl_3$ at 130—140°, is reduced (Clemmensen) to 1 : 2 : 3 : 4-$C_6H_2Et(OH)_3$, which gives, as above, 7 : 8-*dihydroxy*-4-*methyl*- (70%), m.p. 205° (*diacetate*, m.p. 174°), and -3 : 4-*dimethyl*- (50%), m.p. 244° (*diacetate*, m.p. 187°), -6-*ethylcoumarin*, 7 : 8-*dihydroxy*-4-*methyl*-3 : 6-*diethyl*- (30%), m.p. 202° (*diacetate*, m.p. 167°), -4-*methyl*-6-*ethyl*-3-n-*propyl*- (25%), m.p. 159° (*diacetate*, m.p. 147°), and -4-*phenyl*-6-*ethyl*- (70%), m.p. 145° (*diacetate*, m.p. 120°), -*coumarin*. The reactivity of (**I**) is reduced by substituents in the order $CO_2H > Ac > CO_2Me > Et$. 7 : 8-Diacetoxy- and 6-acetoxy-coumarins (cf. below) and chromones do not undergo Fries rearrangement.

XVI. Reactivity of quinol in the von Pechmann reaction is completely repressed by 2-Br or -Ac, partly repressed by 2-Cl, but increased by 2-Me or -Et. Thus there are obtained in 73% H_2SO_4 6-*hydroxy*-4-*methyl*- (**III**) (30%), m.p. 240° (*Me ether*, m.p. 169°; CO_2Me-derivative, m.p. 139°; *benzoate*, m.p. 125°), -4-*methyl*-7-*ethyl*- (45%), m.p. 200° (*acetate*, m.p. 133°), -3 : 4-*dimethyl*-7-*ethyl*- (40%), m.p. 239° (*acetate*, m.p. 150°), -4-*methyl*-3 : 7-*diethyl*- (35%), m.p. 229° (*acetate*, m.p. 102°), -4-*methyl*-7-*ethyl*-3-n-*propyl*- (5—10%), m.p. 218°, -4-*phenyl*-7-*ethyl*- (15%), m.p. 194°, -4 : 7-*dimethyl*- (70%), m.p. 208° (*acetate*, m.p. 207°), -3 : 4 : 7-*trimethyl*- (45%), m.p. 267° (*acetate*, m.p. 189°), -4 : 7-*dimethyl*-3-*ethyl*- (25%), m.p. 242° (*acetate*, m.p. 153°), -4 : 7-*dimethyl*-3-n-*propyl*- (20%), m.p. 236° (*acetate*, m.p. 102°), and -4-*phenyl*-7-*methyl*- (45%), m.p. 250° (*acetate*, m.p. 202°, -*coumarin* and 7-*chloro*-6-*hydroxy*-4-*methylcoumarin* (20%), m.p. 198° (*acetate*, m.p. 182°). $CH_2Bz{\cdot}CO_2Et$ does not condense with quinol or its 2-Br, -Cl, or $-CH_2Bz$ derivatives. 2 : 1 : 4-$C_6H_3Ac(OH)_2$, best (60%) obtained by Fries rearrangement, gives (Clemmensen) 55% of 2 : 1 : 4-$C_6H_3Et(OH)_2$, m.p. 112°. 6-*Hydroxy*-5-*benzeneazo*-4-*methylcoumarin*, m.p. 285°, readily obtained from (**III**), could not be converted into the 5 : 6-$(OH)_2$-compound, nor could the 5-NO_2-compound. R. S. C.

Colouring matter of the flowers of *Tagetes patula*: isolation of a new flavonol, patuletin, and its constitution. P. Suryaprakasa Rao and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, **14, A**, 643—647).—The EtOH extract of the petals with H_2O gives *patuletin* (**I**), $C_{15}H_{10}O_7$, m.p. 262—264° [Ac_5 derivative, m.p. 170—172°; Me_5 *ether*, m.p. 158—159° (sinters at 143°)]. Alkaline oxidation of (**I**) affords protocatechuic acid. The resemblance to quercetagetin suggests OH in positions 5 and 6. (**I**) is possibly 3 : 5 : 6 : 3′ : 4′-pentahydroxyflavone. W. C. J. R.

Cannabis indica. **IX. Isolation of 3′ : 4′ : 5′ : 6′-tetrahydrodibenzopyran derivatives from pulegone–orcinol and pulegone–olivetol condensation products. Synthesis of *d*-tetrahydrocannabinol. X. Essential oil from Egyptian hashish.** J. L. Simonsen and A. R. Todd (*J.C.S.*, 1942, 185—188, 188—191).—IX. Acetylation of the resin from pulegone–orcinol condensation (cf. Ghosh *et al.*, A., 1941, II, 145; Adams *et al.*, *ibid.*, 331) gives 6″-acetoxy-2 : 2 : 5′ : 4″-tetramethyl-3′ : 4′ : 5′ : 6′-tetrahydrodibenzopyran (**I**), m.p. 123°, $[\alpha]_D^{21}$ +30·4° in $CHCl_3$, and the remaining resin is dextrorotatory and similar in composition to the deacetylated substance. *d*-5-Hydroxy-5′ : 7-dimethyl-3 : 4-*cyclo*hexenocoumarin, prepared from *d*-methyl*cyclo*hexan-3-one with orcinol–H_2SO_4, affords (Grignard reaction) d-6″-*hydroxy*-2 : 2 : 5′ : 4″-*tetramethyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzopyran*, m.p. 104—105°, $[\alpha]_D^{10\cdot7}$ +161° in $CHCl_3$, which is obtained, $[\alpha]_D^{20}$ ~ +42°, by hydrolysing (**I**). The pulegone–olivetol product with *l*-menthoxyacetyl chloride yields a mixture from which can be separated d-*tetrahydrocannabinol* l-*menthoxyacetate*, m.p. 76°, $[\alpha]_D^{24}$ +51·9° in $CHCl_3$. d-5-*Hydroxy*-5′-*methyl*-7-n-*amyl*-3 : 4-*cyclohexenocoumarin*, m.p. 145—148°, $[\alpha]_D^{24}$ +130·3° in $CHCl_3$ (*acetate*, m.p. 76—77°, $[\alpha]_D^{22}$ +132·9° in $CHCl_3$), prepared from olivetol, with MgMeI forms d-*tetrahydrocannabinol*, b.p. 160°/10⁻³ mm., $[\alpha]_D^{20}$ +134·8° in $CHCl_3$, which gives the *l*-menthoxyacetate, $[\alpha]_D^{25}$ +62·16° in $CHCl_3$. The l-*menthoxyacetate* of *dl*-tetrahydrocannabinol has m.p. 56—57°, $[\alpha]_D^{17\cdot5}$ −53·7° in $CHCl_3$.

X. The "low-boiling terpene" fraction from the oil is mainly *p*-cymene together with an unidentified optically active constituent and *p*-$C_6H_4Me{\cdot}CMe{:}CH_2$ [oxidised to *p*-$C_6H_4Me{\cdot}COMe$ (2 : 4-*dinitrophenylhydrazone*, m.p. 252—253°)]; from one fraction a *hydrochloride*, $C_{10}H_{17}Cl$, b.p. 110—120°/21 mm., has been isolated. From the "higher-boiling terpene" fraction, α-caryophyllene has been isolated. A hypothetical scheme for the biogenesis of cannabinol etc. is discussed. F. R. S.

Vinylene homologues of triphenylmethane dyes.—See A., 1942, II, 194.

Vat dyes derived from diphenylene oxide, sulphide, etc.—See B., 1942, II, 149.

2 : 3 : 4 : 5-Tetrahydrothiophen 1 : 1-dioxide.—See B., 1942, II, 145.

5-Iodo-4 : 6-diketo-2-methyltetrahydropyridine-1-acetic acid.—See B., 1942, III, 114.

Germicidal activity of some quaternary ammonium salts. H. G. Kolloff, A. P. Wyss, R. E. Himelick, and F. Mantele (*J. Amer. Pharm. Assoc.*, 1942, **31**, 51—53).—The following were prepared by the method of Knight and Shaw (A., 1938, II, 291): 1-*tetradecyl-pyridinium bromide*, m.p. 54·5—55·5° and 198°; 1-*dodecyl-α-picolinium chloride*, m.p. 94·5—95·5° and 141°, *bromide*, m.p. 123—124°, and *iodide*, m.p. 130—131°; 1-*tetradecyl-α-picolinium chloride* (extremely hygroscopic), *bromide*, m.p. 125—126° and 192·5°, and *iodide*, m.p. 130—131° and 146·5°; 1-*cetyl-α-picolinium chloride* (extremely hygroscopic), *bromide*, m.p. 123·5—124·5° and 214°, and *iodide*, m.p. 119—120° and 201°; 1-*dodecyl-γ-picolinium chloride*, m.p. 61—63°, *bromide*, m.p. 66—67°, and *iodide*, m.p. 61·5—62°; 1-*tetradecyl-γ-picolinium chloride*, m.p. 73—74°, *bromide*, m.p. 79—80°, and *iodide*, m.p. 74—75°; 1-*cetyl-γ-picolinium chloride*, m.p. 81—82° and 104—105°, *bromide*, m.p. 84·5—85·5° and 110°, and *iodide*, m.p. 67—68° and 110—110·5°. All m.p. are corr. (Cf. A., 1942, III, 481.) F. O. H.

Pyridyl-3-aldehyde, pyridyl-3-carbinol, and pyridyl-3-acrylic acid. L. Panizzon (*Helv. Chim. Acta*, 1941, **24**, 24—28E).—Nicotinhydrazide is converted by $PhSO_2Cl$ in C_5H_5N at ~25° into its *PhSO*$_2$'derivative, m.p. 183—184°, transformed by dry Na_2CO_3 in $(CH_2{\cdot}OH)_2$ at 160° into pyridyl-3-aldehyde (**I**), b.p. 85—90°/13 mm. (*NaHSO*$_3$ compound, m.p. 157°; *semicarbazone*, m.p. 213—214°; *methiodide*, m.p. 174°; very hygroscopic *methochloride*, m.p. 105°). (**I**) is very hygroscopic and not readily oxidised; its aq. solution is stable for several days. It is converted by HCl–EtOH at room temp. into *pyridyl-3 Et*$_2$ *acetal*, b.p. 118—120°/15 mm. Catalytic hydrogenation (Rupe Ni in abs. EtOH at 40°) leads to *pyridyl-3-carbinol*, b.p. 144—145°/16 mm. (*picrate*, m.p. 158°; *benzoate*, b.p. 196—198°/17 mm., and its *hydrochloride*, m.p. 116°, *methiodide*, m.p. 159°, and *methochloride*, m.p. 49°). (**I**), $CH_2(CO_2H)_2$, C_5H_5N, and a little piperidine at 100° afford *pyridyl-3-acrylic acid*, m.p. 233° (*amide*, m.p. 148°; very hygroscopic *diethylamide*, b.p. 145°/0·1 mm.; *Et* ester, b.p. 156—158°/14 mm., and its *methiodide*, m.p. 147°). H. W.

Pyridine-3-acetic acid (β-homonicotinic acid). M. Hartmann and W. Bosshard (*Helv. Chim. Acta*, 1941, **24**, 28—35E).—3-Pyridyl Me ketone is converted by $(NH_4)_2S$ and S at 160—200° into a mixture of *pyridine-3-acetic acid* (**I**), m.p. 144°, and its *amide* (**II**), m.p. 123°. If the reaction is effected in presence of dioxan it is possible to isolate (**II**) by crystallisation but the separation is tedious and (**II**) is preferably obtained by the action of aq. NH_3 on *Me pyridine-3-acetate* (**III**), b.p. 112°/12 mm. (**I**) is best obtained by esterifying the crude mixture with HCl–MeOH and hydrolysing (KOH–MeOH) the distilled ester. (**I**) gives a well-cryst. *hydrochloride*, m.p. 152—155°, and *nitrate*, m.p. 112—115°, and an *Et* ester, b.p. 122°/13 mm. Treatment of (**III**) with the requisite higher alcohol and HCl gives the corresponding *Pr*$^{\alpha}$, b.p. 140°/10 mm., *Pr*$^{\beta}$, b.p. 134°/10 mm., *Bu*$^{\beta}$, b.p. 142°/13 mm., and *allyl*, b.p. 138°/14 mm., ester. *Pyridine-3-acetdiethylamide* has b.p. 175°/12 mm. (**III**) yields a *picrate*, m.p. 128—130°, *methiodide* (**IV**), m.p. ~90°, and *methochloride* which solidifies in a freezing mixture; it immediately yields quaternary salts with Me_2SO_4 and *p*-$C_6H_4Me{\cdot}SO_3Me$ but only slowly gives non-cryst. compounds with EtBr and MeCl. (**IV**) is transformed by Ag_2O in aq. solution into *pyridine-3-acetic acid Me betaine* ($+1H_2O$), m.p. 130—132° (decomp.) [*hydrochloride*, m.p. 167° (decomp.); *picrate*, m.p. 154—156°]. (**III**) is hydrogenated (Pt in EtOH–AcOH) to *Me piperidine-3-acetate acetate*, m.p. 115—118°, transformed by HCO_2H and CH_2O into *Me 1-methylpiperidine-3-acetate*, b.p. 96°/13 mm. (*picrate*, m.p. 112—115°). CH_2 of (**I**) retains activity but, unlike $CH_2Ph{\cdot}CO_2H$, (**I**) does not undergo the Perkin synthesis with PhCHO. (**III**) and PhCHO in presence of Na give *Me α-3-pyridylcinnamate*, b.p. 157°/0·2 mm., hydrolysed to the *acid*, m.p. 233°. (**I**) or (**II**) gives a dark violet-brown colour with 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$, a yellow colour with CNBr and NH_2Ph; with CNBr and *p*-$NH_2{\cdot}C_6H_4Ac$ (**I**) gives a yellow and (**II**) an orange-rose colour. The pharmacological action of some of these compounds is described. H. W.

Halogenation of isatin-α-chlorides. E. Kambli (*Helv. Chim. Acta*, 1941, **24**, 93—99E).—The isatin derivative, suspended in C_6H_6 or PhCl, is transformed by PCl_5 into the isatin-α-chloride (**I**) (compounds with a double linking between the N and vicinal C of the heterocyclic ring are termed α-derivatives), which is converted by SO_2Cl_2 or Br into the halogenated derivative; as these are unusually sensitive, particularly towards moisture, they are coupled with a hydroxythionaphthen or 4-substituted α-$C_{10}H_7{\cdot}OH$ to the indigoid dye. The halogen atom enters (**I**) exclusively at $C_{(5)}$ and substitution at $C_{(7)}$ has not been observed. Halogenation, therefore, can only occur when H is attached to $C_{(5)}$ and appears to depend also on the presence of other substituents occurring readily when Alk or OAlk is attached to $C_{(4)}$ and markedly less readily when Cl is there present. With unsubstituted isatins chlorination or bromination does not take place. The following compounds have been prepared: 4-*chloro-* and 4-*bromo-2-naphthalene-5′-chloro-7′-methoxy-4′-methyl-2′-indoleindigotin*; 6-*chloro-4-methyl-2-thionaphthen-5′-chloro-7-methyl-2′-indoleindigotin*; 4-*chloro-2-naphthalene-5′-chloro-4′* : *7′-dimethyl-2′-indoleindigotin*; 4-*chloro-2-naphthalene-4′* : *5′-dichloro-7′-methoxy-2′-indoleindigotin*; 4-*chloro-2-naphthalene-5′* : *7′-dichloro-4′-methyl-2′-indoleindigotin*. H. W.

2-Amino-8-hydroxyquinoline.—See B., 1942, II, 97.

Pyrroketones. III. Synthesis of an opsopyrrole ketone and of 3 : 4-dichloropyrrole. H. Fischer and K. Gangl [with, in part, Reinecke] (*Z. physiol. Chem.*, 1941, **267**, 188—200).—Addition of 3 : 4-dichloro-5-carbethoxypyrrole-2-carboxyl chloride (**I**) to a Grignard solution prepared by the addition of cryptopyrrole to Mg and EtBr in Et_2O leads to *Et* 3 : 4-*dichloro-3′* : *5′-dimethyl-4′-ethylpyrroketone-5-carboxylate* (**II**), m.p. 203° (*hydrazidohydrazone*, m.p. 225°; corresponding *acid*, m.p. 249°), converted by Br in AcOH into 3 : 4-dichloro-5-carbethoxypyrrole-2-carboxylic acid, decomp. 275°. (**II**) is transformed by SO_2Cl_2 in abs Et_2O into *Et*$_2$ 3 : 4-*dichloro-3′-methyl-4′-ethylpyrroketone-5* : *5′-dicarboxylate*, m.p. 201—202°. Cryptopyrrolecarboxylic acid is transformed by (**I**) and $AlCl_3$ in CS_2 into 3 : 4-*dichloro-5-carbethoxy-3′* : *5′-dimethylpyrroketone-4′-propionic acid*, m.p. 210—211°. (**I**) and the Grignard compound from opsopyrrole afford *Et* 3 : 4-*dichloro-3′-methyl-4′-ethylpyrroketone-5-carboxylate*, m.p. 184°, which is hydrolysed and decarboxylated by 10% NaOH at 190—200° to 3 : 4-*dichloro-3′-methyl-4′-ethylpyrroketone*, m.p. 156°. *Et*$_2$ 3 : *3′-dimethyl-4* : *4′-diethylpyrroketone-5* : *5′-dicarboxylate*, m.p. 202°, is hydrolysed by NaOH in boiling aq. EtOH to the acid (**III**), which is decarboxylated at 180°/high vac. to 3 : *3′-dimethyl-4* : *4′-diethylpyrroketone* (*opsopyrrole ketone*) (**IV**), m.p. 166°. 5 : *5′-Dibromo-3* : *3′-dimethyl-4* : *4′-diethylpyrroketone*, decomp. 179°, is obtained from Br and (**III**) in AcOH or (**IV**) in Et_2O. (**IV**) could not be oxidised to a pentduopent compound. *Et*$_2$ 3 : 4-dichloropyrrole-2 : 5-dicarboxylate is hydrolysed and decarboxylated by 10% NaOH at 160—170° to 3 : 4-*dichloropyrrole*, m.p. 74°, converted by $OMe{\cdot}CH_2Cl$ into a substance with porphyrin spectrum. Treatment of the ketone $C_{31}H_{36}O_3N_4$ (**V**) (Fischer and Adler, A., 1932, 627) appears to give in variable yield a dihydrobromide. (**V**) is probably the ketone of 5-hydroxy-3′ : 4-dimethyl-3 : 4′-diethylpyrromethene (**VI**); this view is supported by its behaviour toward PhN_2Cl. When heated for a short time in boiling *m*-$C_6H_4(OH)_2$ (**V**) gives a *compound*, $C_{37}H_{44}O_5N_4$, m.p. 238° after softening at 330°, and (**VI**). H. W.

Pyrazolone derivatives. F. X. Demers and E. V. Lynn (*J. Amer. Pharm. Assoc.*, 1941, **30**, 627—628).—3 : 4 : 1-$NO_2{\cdot}C_6H_3(NH_2){\cdot}OEt$ [from the 4-NHAc-compound (**I**)] is diazotised (HBF_4–$NaNO_2$) and converted ($NaNO_2$–Cu) into 3 : 4-*dinitrophenetole* (poor yield), m.p. 76°. Reduction ($FeSO_4$–aq. NH_3) of (**I**) affords 3-*amino-4-acetamido-*, m.p. 139—140°, acetylated to 3 : 4-*diacetamido-phenetole*, m.p. 186°. Diazotisation of 4 : 2 : 1-$NO_2{\cdot}C_6H_3(NH_2){\cdot}OEt$ followed by treatment with $Na_2S_2O_5$ affords 5-*nitro-2-ethoxyphenylhydrazine*, m.p. 124·5—125·5° (corresponding *benzaldehyde-*, m.p. 169—169·5°, and *acetone-hydrazone*, m.p. 123·5—124°), which, with $CH_2Ac{\cdot}CO_2Et$, gives 1-(5-*nitro-2-ethoxyphenyl*)-3-*methyl-5-pyrazolone*, m.p. 82—83·5°. F. O. H.

Pyrazolones.—See B., 1942, II, 145, 187.

Pyrazoles.—See B., 1942, II, 176.

Preparation of histidine by means of 3 : 4-dichlorobenzenesulphonic acid. H. B. Vickery (*J. Biol. Chem.*, 1942, **143**, 77—87).—3 : 4 : 1-$C_6H_3Cl_2{\cdot}SO_3H$, m.p. 71—72° ($+2H_2O$) (modified prep.), added to a cold conc. aq. solution (p_H 1·2) of the hydrolysis products of coagulated red blood cells, affords *histidine di-3* : *4-dichlorobenzenesulphonate* (**I**), decomp. ~280°, together with some more sol. leucine mono-3 : 4-dichlorobenzenesulphonate (**II**), which can be removed by careful crystallisation, with seeding with pure (**I**), and decanting the solution containing (**II**). Histidine (**III**) is recovered from (**I**) by aq. $Ba(OH)_2$, and from fairly pure preps. of red blood cells the equiv. of >6% of (**III**) is obtained. A. T. P.

Ammonolysis of benzil by liquid ammonia. W. B. Leslie and G. W. Watt (*J. Org. Chem.*, 1942, **7**, 73—78).—The action of liquid NH_3, alone and in presence of NH_4Cl or KNH_2, on Bz_2 at 103° and at 35° has been investigated and methods for the separation and determination of the products have been elaborated. Lophine (**I**) is not formed in reactions effected near room temp. Imabenzil and benzilimide do not appear as products of reactions conducted at 103°. Triphenyloxazole is not produced in reactions involving KNH_2. The yield of (**I**) is a function of [NH_4Cl]. H. W.

Derivatives of amytal, pentobarbital, and dial. Optical crystallographic study. M. E. Hultquist, C. F. Doe, and N. F. Witt (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 219).—The p-*bromo-* and p-*chlorobenzyl* derivatives are described of amytal (5-ethyl-5-*iso*amylbarbituric acid) [the m.p. (uncorr.) are given in that order] (133°, 102—105°), of pentobarbital (5-ethyl-5-α-methylbutylbarbituric acid) (114°, 111°), and of dial (5 : 5-diallylbarbituric acid) (132·5°, 125—134°). Optical data are presented on the above, and on the parent substances and the *p*-nitrobenzyl derivatives, including the optical sign, the elongation, n^{25} on the *α-*, *β-*, and *γ-*axes, the rhombic dispersion, and the crystal system. J. D. R.

Thiobarbituric acids.—See B., 1942, III, 142.

6-Amino-6-piperidinopyridines.—See B., 1942, II, 145.

Indazoles.—See B., 1942, II, 131.

Reactions of methylenediamines as ammonoaldehydes. J. R. Feldman and E. C. Wagner (*J. Org. Chem.*, 1942, **7**, 31—47).—The structural analogy between hydrated CH_2O (I) and methylenediamines (II), considered as NH_3-system aldehydes, is proved by experimental demonstrations of a clear functional analogy established by realising with (II) or (I), used interchangeably, reactions characteristic of (I). In each reaction studied both reagents lead to the formation of the same principal product; the by-product of the NH_3-system reaction is the liberated amine, corresponding with the H_2O eliminated when CH_2O is used. To exclude the possibility that small amounts of H_2O, operating cyclically, cause hydrolysis of (II) and liberation of CH_2O as actual reactant, several reactions have been effected under anhyd. conditions. The reactions are attributable to the essentially aldehydic character of the group $:N\cdot CH_2\cdot N:$. 3-*p*-Tolyl-6-methyl-1 : 2 : 3 : 4-tetrahydroquinazoline, m.p. 139—141°, is obtained from *p*-$C_6H_4Me\cdot NH\cdot CH_2\cdot C_6H_3Me\cdot NH_2$-3 : 6 and methylenedi-*p*-toluidine (**III**), -*p*-chloroaniline (**IV**), -*p*-bromoaniline (**V**), -*p*-anisidine (**VI**), -ethylaniline (**VII**), -piperidine (**VIII**), and -morpholine (**IX**) in hot EtOH or under anhyd. conditions; the change is unfavourably affected by NaOEt. The requisite anthranilanilide is converted by short warming at ~60° with NaOH and CH_2O in EtOH or by prolonged boiling with (**III**)—(**IX**) in abs. EtOH into 3-p-*bromophenyl*-, m.p. 199—200° (corr.), 3-p-*anisyl*-, m.p. 185—185·5°, and 3-*phenyl*- (**X**), m.p. 180° (corr.), -1 : 2 : 3 : 4-*tetrahydroquinazol*-4-*one*, identified by oxidation to 3-*p*-bromophenyl-, m.p. 190—190·5°, 3-p-*anisyl*-, m.p. 193—194°, and 3-phenyl-, m.p. 138—139°, -3 : 4-dihydroquinazol-4-one, obtained also synthetically. If the prep. of (**X**) is attempted at a lower temp. and with relatively more CH_2O the product is 3-*phenyl*-1-*hydroxymethyl*-1 : 2 : 3 : 4-*tetrahydroquinazol*-4-*one*, m.p. 110—111° (corr.), which passes when heated into (**X**) and CH_2O. *o*-$NH_2\cdot C_6H_4\cdot CO\cdot NH_2$ and CH_2O yield 1 : 3-*dihydroxymethyl*-1 : 2 : 3 : 4-*tetrahydroquinazol*-4-*one*, m.p. 141°, which loses CH_2O when heated alone or with H_2O, EtOH, or aq. NH_3 and is oxidised by $KMnO_4$ in $COMe_2$ to 3 : 4-*dihydroquinazol*-4-*one*, m.p. 210—212° (*picrate*, m.p. 206—208°), identical with the product obtained from *o*-$NH_2\cdot C_6H_4\cdot CO_2H$ and HCO·NHPh. The requisite phenol and (**III**), (**IV**), or (**VIII**) in boiling EtOH give the following: 2-*piperidinomethyl*-1-*naphthol*, m.p. 133·5—134·5° (*hydrochloride*, m.p. 242·4°), 1-*piperidinomethyl*-2-*naphthol*, m.p. 95—96·5° (*hydrochloride*, m.p. 239—241°), 1-p-*toluidinomethyl*-, m.p. 136·5—137°, and 1-p-*chloroanilinomethyl*-, m.p. 139—141·5°, -2-*naphthol*, and *pipcridinomethylcarvacrol*, m.p. 182—183° (*hydrochloride*, m.p. 235—239°). These exhibit a partly cryptophenolic character since they are insol. in cold aq. alkali but dissolve when heated. In the presence of alkali the reaction proceeds farther; thus β-$C_{10}H_7\cdot OH$ and (**III**) give methylenedinaphthol, m.p. 197—198°. $NPhMe_2$ and (**VIII**) do not react in abs. EtOH but in presence of HCl $CH_2(C_6H_4\cdot NMe_2)_2$ is produced with liberation of the equiv. amount of piperidine (**XI**). Carbazole with CH_2O or (**VIII**) in AcOH gives methylenedicarbazole, m.p. 301—303°, but if it is heated with (**XI**) and CH_2O in aq. EtOH in absence of acid the product is 9-*piperidinomethylcarbazole*, m.p. 99—99·5°. *N*-Piperidinomethylphthalimide, m.p. 119—119·5°, is obtained from *o*-$C_6H_4(CO)_2NH$ (**XII**), (**XI**), and CH_2O or from (**XII**) and (**VIII**) in boiling EtOH. *N*-Piperidinomethylsuccinimide, m.p. 107—107·5°, is prepared similarly. In these reactions the imides must be regarded as weak acids, the acid character of which is increased in basic media. Dimethyldihydroresorcinol and (**III**), (**IV**), (**V**), and (**VI**) give high yields of methylenedi-4 : 4-dimethyl*cyclo*hexa-2 : 6-dione, identical with the compound obtained from methone and CH_2O. H. W.

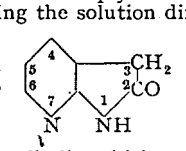
Phenazines etc.—See B., 1942, II, 150.

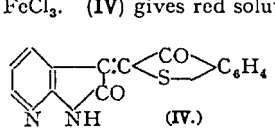
Relationship of the dyeing properties of *NN'*-dialkyl-2 : 2'-dipyrazoleanthronyls to the character of the alkyl groups. J. Koch (*Helv. Chim. Acta*, 1941, **24**, 187—197E).—*NN'*-Dialkyl-2 : 2'-dipyrazoleanthronyls, (**I**) or (**II**), give dyeings which change to a remarkable extent under the influence of soap. The effect diminishes as the size of R increases and disappears when R = *n*-amyl. It is not observed when alkyl is replaced by a suitable alkoxyalkyl residue, *e.g.*, ·$[CH_2]_2$·OEt. As the length of alkyl chain following O increases, the whole group approximates to *n*-alkyl in character. Thus when R = ·$[CH_2]_2$·OBu^α the character of the dye is intermediate between those in which R = Bu^α and *n*-C_5H_{11}. A similar effect is produced by branching of the alkyl chain provided that the group is attached to N by a *sec.*-C; thus Bu^β behaves like an *n*-alkyl. The further the length of one branch increases, the more the group simulates *n*-alkyl. The *cyclo*hexyl residue behaves as a *sec.*-alkyl residue. *Dyes* are described in which the R are respectively: CH_2Pr^β, CH_2Pr^β; Me, Me; Et, Et; Pr^α, Pr^α; Bu^α, Bu^α; Et, CH_2Ph; Me, CH_2Ph; C_5H_{11}, C_5H_{11}; allyl, allyl; ·$[CH_2]_2$·OBu^α, ·$[CH_2]_2$·OBu^α; ·$[CH_2]_2$·OEt, ·$[CH_2]_2$·OEt; ·$[CH_2]_2$·OMe, ·$[CH_2]_2$·OMe; Pr^β, *cyclo*hexyl; Pr^β, Pr^β; Pr^β, Bu^β; Bu^β, Bu^β; *sec.*-C_5H_{11}, *sec.*-C_5H_{11}; CH_2Ph, ·$[CH_2]_2$·OEt; CH_2Ph, ·$[CH_2]_2$·OMe; Me, ·$[CH_2]_2$·OEt; Et, ·$[CH_2]_2$·OEt; Me, ·$[CH_2]_2$·OMe; Et, ·$[CH_2]_2$·OEt; Et, *cyclo*hexyl; Me, *cyclo*hexyl; CH_2Ph, Pr^β; Me, Pr^β; Et, Pr^β; ·$[CH_2]_2$·OEt, *cyclo*hexyl; ·$[CH_2]_2$·OMe, *cyclo*hexyl; ·$[CH_2]_2$·OEt, Pr^β; ·$[CH_2]_2$·OMe, Pr^β. H. W.

Attempts to find new antimalarials. XVIII. Derivatives of *m*-phenanthroline. W. O. Kermack and W. Webster (*J.C.S.*, 1942, 213—218).—Addition of Et β-3-acetamidoanilinoacrotonate to paraffin at 270° gives 5-*acetamido*-4-*hydroxy*-2-*methylquinoline*, m.p. 236°, hydrolysed (HCl) to the 5-NH_2-compound, m.p. 210°, which is converted (Skraup) into 4-*hydroxy*-2-*methyl*-5 : 6 : 2' : 3'-*pyridoquinoline*, m.p. 142°. This with PCl_5 affords the 4-*Cl*-derivative, m.p. 140°, not identical with 4-*chloro*-2-*methyl*-7 : 8 : 2' : 3'-*pyridoquinoline*, m.p. 190°, prepared from the corresponding OH-compound. The Skraup synthesis on 7-amino-2-hydroxy-4-methylquinoline yields 2-*hydroxy*-4-*methyl*-7 : 8 : 2' : 3'-*pyridoquinoline*, m.p. 318°, which with PCl_5 gives the 2-*Cl*-compound, m.p. 161°. *m*-$C_6H_4(NH_2)_2$ and Et oxaloacetate form *Et* 7-*amino*-2-*hydroxyquinoline*-4-*carboxylate*, m.p. 262°, saponified (KOH) to the *acid*, m.p. >400°, which is decarboxylated to 7-amino-2-hydroxyquinoline. This substance in the Skraup synthesis gives 2-hydroxy-, which with PCl_5 gives 2-*chloro*-7 : 8 : 2' : 3'-*pyridoquinoline*, m.p. 166°. 2-*Hydroxy*-, m.p. 315°, is similarly converted into 2-*chloro*-5 : 6 : 2' : 3'-*pyridoquinoline* (**I**), m.p. 147—148°. In MeOH solution, *m*-phenanthroline and Me_2SO_4 afford 5 : 6 : 2' : 3'-*pyridoquinolinium methosulphate*, m.p. 192°, but the base and Me_2SO_4 warmed together yield 1-methyl-5 : 6 : 2' : 3'-pyridoquinolinium methosulphate, which after oxidation [alkali–$K_3Fe(CN)_6$] and treatment with PCl_5 gives (**I**).

The following compounds are obtained by heating the appropriate chloropyridoquinolines and bases with a trace of Cu: 4-(β-diethylaminoethylamino)-2-methyl-5 : 6 : 2' : 3'- (*dipicrate*, m.p. 237°), 4-(δ-diethylamino-α-methylbutylamino)-2-methyl-5 : 6 : 2' : 3'- (*dipicrate*, m.p. 195°), 4-(*β-diethylaminoethylamino*)-2-*methyl*-7 : 8 : 2' : 3'-, m.p. 115—116° (*trihydrobromide*, m.p. 284—285°), 4-(δ-diethylamino-α-methylbutylamino)-2-methyl- (*tripicrate*, m.p. 130°), 2-(*β-diethylaminoethylamino*)-4-*methyl*-7 : 8 : 2' : 3'-, m.p. 113—114° [*dihydrobromide*, m.p. 281—283° (decomp.)], 2-(δ-diethylamino-α-methylbutylamino)-4-methyl-7 : 8 : 2' : 3'- [*monopicrate*, m.p. 260° (decomp.)], 2-(β-diethylaminoethylamino)-5 : 6 : 2' : 3'- (*dipicrate*, m.p. 223—224°), and 2-(δ-diethylamino-α-methylbutylamino)-5 : 6 : 2' : 3'-pyridinoquinoline (*dipicrate*, m.p. 195°). F. R. S.

7-Pyroxindole, 7-pyrisatin, and 7 : 7'-dipyrindigotin. H. Kägi (*Helv. Chim. Acta*, 1941, **24**, 141—150E).—2-Amino-3-diazoacetylpyridine (**I**) passes in $NPhMe_2$ at 125—180° into N_2 and 7-*pyroxindole* (**II**), m.p. 175°, converted by HNO_2 into 7-*pyrisatin*-3-*oxime* (**III**), m.p. 252—254°. This is reduced by Sn and acid to 3-amino-7-pyroxindole [*mono*- and *di*-, m.p. 201° (decomp.), -*hydrochloride*; *dihydrobromide*, m.p. 197° (decomp.)]. The salts are oxidised by $FeCl_3$ to 7-*pyrisatin* (**IV**), m.p. 225—230° after becoming black at 190°, more simply obtained by reducing (**III**) with Zn dust and oxidising the solution directly with $FeCl_3$. (**IV**) gives red solutions

(II.) 


(IV.)

in dil. alkalis which soon become colourless and when acidified give 7-*pyrisatoic* [2-*aminopyridine*-3-*glyoxylic*] *acid*, decomp. 197—199°, which is not readily reconverted into (**IV**). With C_6H_6 containing thiophen and conc. H_2SO_4 (**IV**) gives a well-defined indophenol reaction. (**IV**) and freshly pptd. 3-hydroxythionaphthen-2-carboxylic acid in warm MeOH containing a little Na_2CO_3 afford *thio*-7-*pyrindigo*-*scarlet* (**V**) which gives a yellow vat from which cotton and wool are dyed scarlet. 7 : 7'-*Dipyrindigotin*, m.p. >290°, is best obtained by heating (**I**) with dil. acid followed by treatment of the ammoniacal solution with air. It is insol. in Na_2CO_3 and dil. NH_3 but sol. in dil. NaOH to a solution from which it cannot be regenerated. The vat is best obtained with $Na_2S_2O_4$ and 5% K_2CO_3. It gives violet shades on wool and cotton which are not fast to dil. acids or caustic alkalis. H. W.

Ammeline derivatives.—See B., 1942, II, 146.

Condensation products of melamine and formaldehyde. A. Gams, G. Widmer, and W. Fisch (*Helv. Chim. Acta*, 1941, **24**, 302—319E).—Analyses are recorded of products withdrawn after definite intervals from a mixture of 30% CH_2O (3·35 mols.) and melamine (**I**) (1 mol.) in aq. NaOH at 70° and p_H ~8·5. The samples are dried over P_2O_5, powdered, and again dried until const. in wt. They are then analysed. They are also hardened at 90° (1 hr.) and 130° (1 hr.) and again analysed. The reaction of (**I**) with varied amounts of CH_2O is also studied. In slightly alkaline or neutral medium (**I**) and CH_2O (6 mols.) give a product with <6 $CH_2\cdot OH$. Hexahydroxymethylmelamine is best obtained in the presence of a little conc. HCl at room temp. It decomposes before melting. It is very sensitive to heat. With MeOH and conc. HCl (**I**) affords *hexa-*

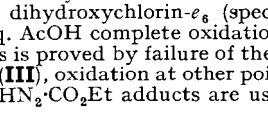
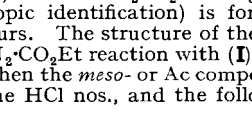
methoxymethylmelamine (**II**), m.p. 55° (corr.), freely sol. in all customary solvents and very stable towards heat. (**II**) is readily re-etherified by the requisite alcohol containing a little HCl. The *Et$_6$ ether* is described. H. W.

Synthesis of a tripyrrylmethene and of a dipyrropyrone. Constitution of prodigiosin. H. Fischer and K. Gangl (*Z. physiol. Chem.*, 1941, **267**, 201—209).—Et 3-hydroxy-5-methylpyrrole-4-carboxylate is converted by $COCl_2$ in boiling PhMe into 2 : 5-*dimethyl*-3 : 4-*dicarbethoxydipyrro-γ-pyrone* (**I**), m.p. 302°. 3-Hydroxy-4-carbethoxy-5-methylpyrrole-2-aldehyde (**II**) and cryptopyrrole under the conditions of a CPh_3 synthesis give 3-*hydroxy*-4′-*carbethoxy*-5 : 3′ : 5′-*trimethyl*-4″-*ethylpyrromethene*, m.p. 204°, whilst (**II**) and 2-aldehydo-4-methyl-3-bromovinylpyrrole-5-carboxylic acid give mainly 3-*hydroxy*-5′-*carboxy*-4-*carbethoxy*-5 : 4′-*dimethyl*-3′-*ω-bromovinylpyrromethene*, m.p. >310°, converted by Br in AcOH into 5′-*bromo*-3-*hydroxy*-4-*carbethoxy*-5 : 4′-*dibromomethyl*-3′-*αββ-tribromoethylpyrromethene hydrobromide*, decomp. 153°. 4-Bromo-2-carbethoxy-3-methyldi-(3-carbethoxy-2 : 4-dimethyl)tripyrrylmethane (**III**) is oxidised by PbO_2 in AcOH to 4-*bromo*-2-*carbethoxy*-3-*methyldi*-(3-*carbethoxy*-2 : 4-*dimethyl*)*tripyrrylmethene* (**IV**), m.p. 216°, reduced by Na in boiling AcOH to (**III**). The *perchlorate*, decomp. ~180°, is reconverted into (**IV**) by NH_3. (**III**) and Br in abs. Et_2O afford 3-*bromo*-5 : 4′-*dicarbethoxy*-4 : 3′ : 5′-*trimethylpyrromethene*, m.p. 132° (*hydrobromide*, m.p. 163°). The synthetic production of a tripyrrylmethene lends support to Wrede's conception of the constitution of prodigiosin (A., 1933, 330, 1232).

[With H. M. Fischer.] Gradual addition of $AlCl_3$ to Et 2-methylpyrrole-5-carboxylate and valeryl chloride in CS_2 leads to *Et* 3-*valeroyl*-2-*methylpyrrole*-5-*carboxylate*, m.p. 123°, catalytically reduced in EtOH at 180—185° to *Et* 2-*methyl*-3-n-*amylpyrrole*-5-*carboxylate*, m.p. 54°, hydrolysed and decarboxylated to 2-*methyl*-3-n-*amylpyrrole*, b.p. 119°/15 mm.

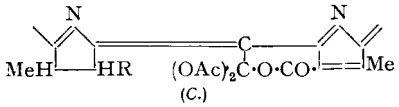
[With Hever.] Et 2 : 4-dimethylpyrrole-3-carboxylate and Et 3-hydroxy-2-aldehydo-5-methylpyrrole-4-carboxylate give a pyrromethene crystallising in unstable, fine needles or yellow-red, stable needles. Only the first variety is obtained from Et 5-aldehydo-2 : 4-dimethylpyrrole-3-carboxylate and Et 3-hydroxy-5-methylpyrrole-4-carboxylate (cf. Fischer and Ley, A., 1923, i, 718). H. W.

Chlorophyll. CX. Phorbide and chlorin-aldehydes and their reactions. H. Fischer and H. Walter (*Annalen*, 1941, **549**, 44—79).—Oxidation of phorbides and chlorins by $KMnO_4$ under sp. conditions effects the reactions, $R{\cdot}CH{:}CH_2 \rightarrow OH{\cdot}CHR{\cdot}CH_2{\cdot}OH \rightarrow RCHO \rightarrow RCO_2H$; of the intermediates, impure $OH{\cdot}CHR{\cdot}CO_2H$ only is isolated in one series. Spectroscopic data are given in detail and discussed, the most important conclusion being that the 2-aldehydes (*A*) thus obtained differ markedly from the 3-aldehydes (*B*) which constitute the *meso*-compounds of the *b*-series. This confirms the differing structure of pyrrole rings I and II postulated by the author. When chlorin-e_6 Me_3 ester (2 g.) is oxidised by $KMnO_4$ in aq. C_5H_5N at room temp. and the product is dissolved in Et_2O, 0·5N-NaOH removes 2-carboxy-2-devinylchlorin-e_6 Me_3 ester, RCO_2H [with CH_2N_2 gives the *Me*$_4$ ester (**I**) (0·3 g.), m.p. 253°, [α] —, 800° (in this and other cases [α] are [α]^{20} for 680—730 mμ. and white light, respectively)]. 5% HCl then removes 2-*αβ-dihydroxy*[" 2-*glycoyl* "]-2-*devinylchlorin*-e_6 *Me*$_3$ ester (**II**) (0·15 g.), m.p. 130°, [α] −198°, +2000°, and 12% HCl removes 2-*formyl*-2-*devinylchlorin*-e_6 *Me*$_3$ ester (**III**) (0·45 g.), m.p. 222°, [α] −111°, —. The relative amounts of (**I**), (**II**), and (**III**) are to some extent controlled by the amount of $KMnO_4$ and temp.; (**I**) and (**III**) are obtained by further oxidation of (**II**). In $COMe_2$–H_2O or C_5H_5N, only dihydroxychlorin-e_6 (spectroscopic identification) is formed; in aq. AcOH complete oxidation occurs. The structure of the products is proved by failure of the $CHN_2{\cdot}CO_2Et$ reaction with (**I**), (**II**), and (**III**), oxidation at other points when the *meso*- or Ac compounds or $CHN_2{\cdot}CO_2Et$ adducts are used, the HCl nos., and the following

(*A*.)  (*B*.) 

reaction: addition of HCN to (**III**) gives an unstable OH-nitrile, converted as usual into the OH-ester, $OH{\cdot}CHR{\cdot}CO_2Me$, which could not be crystallised, but is spectroscopically identified with a by-product accompanying (**I**). HI–AcOH at 50° isomerises (**III**) to 2-*formyl*-2-*de-ethylchloroporphyrin*-e_6 *Me*$_3$ ester, m.p. 273° (oxime). In C_5H_5N, (**III**) gives an *oxime*, m.p. 155°, [α] −700°, −1000° [reconverted into (**III**) by hydrolysis], which in boiling Ac_2O–NaOAc gives 2-*cyano*-2-*devinylchlorin*-e_6 *Me*$_3$ ester, m.p. 230°, resistant to hydrolysis. The phæophorbide derivatives are not obtained by direct oxidation, but in poor yield by ring-closure of the chlorin-e_6 compounds. Thus, in boiling KOH–MeOH–C_5H_5N, (**III**) gives 2-*formyl*-2-*devinylphæophorbide*-a *Me*$_2$ ester (**IV**), m.p. 247° (oxime; red phase test); the corresponding 2-CO_2Me- and 2-$OH{\cdot}CH{\cdot}CH_2{\cdot}OH$ derivatives are spectroscopically identified after ring-closure of (**I**) and (**II**). No cryst. Mg derivative could be obtained from (**IV**) or the Et_2 ester, probably owing to interference by the CHO. Oxidation of phæophorbide-*a* Me_2 ester gives 2-*αβ-dihydroxyethyl*- (**V**) (30%), m.p. 252°, [α] −400°, −500° (dibenzoate), 2-*formyl*- (**VI**) (10%), m.p. 168°, [α] —, +1500° (*dioxime*, m.p. >350°, [α] −400°, +800°), and, after methylation, 2-*carbomethoxy*-2-*devinylphæophorbide*-a *Me*$_2$ ester (**VII**) (15%), m.p. 266°. Oxidation of (**V**) gives (**VII**) and (**VI**). (**VII**) is also obtained by ring-closure of (**I**) by Na_2CO_3–C_5H_5N. Chlorin-e_4 Me_2 ester gives 2-*αβ*-dihydroxyethyl-, not cryst., 2-*formyl*-, m.p. 193°, [α] −443°, +2200° (oxime), and 2-*carbomethoxy*-, m.p. 194°, [α] —, +2200°, -*chlorin*-e_4 *Me*$_2$ ester. *iso*Chlorin-e_4 Me_2 ester (**VIII**) gives 2-*αβ*-dihydroxyethyl-, not cryst., 2-*formyl*- (**IX**), m.p. 221°, [α] +170°, +1800° [anti-*oxime*, m.p. 190° (*acetate*, m.p. 171°), not dehydrated], and 2-*carbomethoxy*-, m.p. 199°, -iso*chlorin*-e_4 *Me*$_2$ ester, all indifferent to $CHN_2{\cdot}CO_2Et$. Ring-closure of (**IX**) by conc. H_2SO_4 at 100° gives a *substance*, m.p. 249°, and a little (**VII**), identified spectroscopically. Interaction of (**IX**) with MgMeI and dehydration of the resulting carbinol at 180°/high vac. regenerates (**VIII**), which is identified spectroscopically. Oxidation of purpurin-7 Me_3 ester gives 2-carbomethoxy- (= purpurin-9), m.p. 232° (decomp.) (and thus impure), 2-*αβ*-dihydroxyethyl-, m.p. 151°, and 2-formyl-, m.p. 142° (oxime), -2-devinylpurpurin-7. Phyllochlorin Me ester gives 2-*formyl*-, m.p. 231°, [α] −1700°, −1300° (oxime), and a little 2-*αβ*-dihydroxyethyl-, m.p. 148°, and non-cryst. 2-carbomethoxy-phyllochlorin Me ester.

[With H. Wenderoth.] With OsO_4 in C_5H_5N–Et_2O, pyrophæophorbide-*a* (not esterified) gives a cryst. adduct, which by boiling with Na_2SO_3 in aq. MeOH and re-esterifying yields the glycol (**V**). Oxidation of (**V**) by AcOH–$Pb(OAc)_4$ is accompanied by decarboxylation, giving the CHO derivative (**VI**). Decarboxylation by $Pb(OAc)_4$ also occurs in the reactions, phæophorbide-*a* → pyrophæophorbide-*a*, and purpurin-7 Me_3 ester → vinylrhodoporphyrin, but mesochlorin-e_6 Me_3 gives an amorphous *product*, $C_{38}H_{42}O_8N_4$, m.p. 117—135°, containing (*C*) (R = $[CH_2]_2{\cdot}CO_2H$).


(*C*.)

R. S. C.

Spectrophotometric studies. IX. Reaction of cyanide with nitrogenous derivatives of ferriprotoporphyrin. D. L. Drabkin (*J. Biol. Chem.*, 1942, **142**, 855—862).—Spectrophotometric data are presented in support of the finding of a general reaction of CN′ with nitrogenous derivatives of ferriprotoporphyrin. In this reaction, as exemplified by the change between CN′ and pyridine ferriprotoporphyrin, 1 equiv. of CN′ per hæmin Fe is sufficient to form a spectroscopically characteristic monocyanide derivative. The reaction may have bearing on the mechanism of CN′ poisoning. The monocyanide derivatives of oxidised hæmochromogens appear to be analogues of cyanomethæmoglobin. The spectroscopic data suggest that on addition of $Na_2S_2O_4$ to solutions of the monocyanide derivatives the corresponding reduced hæmochromogens are obtained. The spectra of the monocyanide derivatives are also very similar to that of dicyanide ferriprotoporphyrin. The last substance is obtained from hæmin in the presence of large amounts of CN′. It is distinguishable spectroscopically from the monocyanide derivatives by the fact that on reduction it affords so-called " reduced cyanide hæmochromogen " or dicyanide ferroprotoporphyrin which has a very characteristic spectrum. H. W.

Morpholines.—See B., 1942, II, 146.

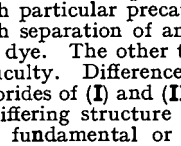
Chemotherapy of bacterial infections. V. Synthesis of 2-*N*^{1}-sulphanilamido-5-alkyl- and 2-*N*^{1}-sulphanilamido-4-methyl-5-alkylthiazoles. K. Ganapathi, M. V. Shirsat, and C. V. Deliwala (*Proc. Indian Acad. Sci.*, 1941, **14**, **A**, 630—635).—The aldehydes $R{\cdot}CH_2{\cdot}CHO$ with SO_2Cl_2 give $R{\cdot}CHCl{\cdot}CHO$, which condense with $CS(NH_2)_2$ to yield the 2-amino-5-alkylthiazoles. Keto-esters, $COMe{\cdot}CHR{\cdot}CO_2Et$, with SO_2Cl_2 yield chloro-keto-esters which hydrolyse to the chloro-ketones $COMe{\cdot}CHClR$. These with $CS(NH_2)_2$ give 2-amino-4-methyl-5-alkylthiazoles. Only 2-*amino*-5-*amylthiazole*, m.p. 72—73°, and 2-*amino*-4-*methyl*-5-iso*amylthiazole*, m.p. 78°, were isolated, the rest being converted directly into the sulphanilamides: 2-N^1-*sulphanilamido*-5-*ethyl*-, m.p. 170° (N^4-*Ac* derivative, m.p. 241—242°), -5-iso*propyl*-, m.p. 217—218° (N^4-*Ac* derivative, m.p. 200—201°), -5-n-*butyl*-, m.p. 246° (N^4-*Ac* derivative, m.p. 211—212°), -5-n-*amyl*-, m.p. 237° (N^4-*Ac* derivative, m.p. 229°), -4-*methyl*-5-*ethyl*-, m.p. 193—194°, -4-*methyl*-5-n-*propyl*-, m.p. 197—198° (N^4-*Ac* derivative, m.p. 236—238°), -4-*methyl*-5-iso*propyl*-, m.p. ?, -4-*methyl*-5-n-*butyl*-, m.p. 192—193° (N^4-*Ac* derivative, m.p. 216—218°), -4-*methyl*-5-n-*amyl*-, m.p. 187—188°, -4-*methyl*-5-iso*amyl*-, m.p. 202—204 (N^4-*Ac* derivative, m.p. 234—236°), and -4-*methyl*-5-n-*hexyl-thiazole*, m.p. 191—192° (N^4-*Ac* derivative, m.p. 216—218°). W. C. J. R.

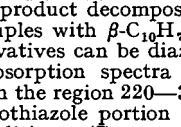
New sulphathiazoles substituted at the nitrogen of the thiazole ring. J. Druey (*Helv. Chim. Acta*, 1941, **24**, 226—233E).—The possibility of amino–imino tautomerism appears important for the biological activity of substituted sulphanilamides. It exists in sulphapyridine, -thiazole, -diazine, -thiodiazole, and -guanidine. 4-Sulphanilamidopyrimidine appears to afford an exception to this generalisation but 4-sulphanilamido-2 : 6-dimethylpyrimidine is

chemotherapeutically very active. Among 3-substituted sulphothiazoles with NH structure the Me derivative is very active; lengthening the chain from Et to Bu causes a diminution in activity, the Bu compound being inactive. The Pr$^{\beta}$ derivative is less active than the Pr$^{\alpha}$ compound. The diminution is probably due to hindrance of resorption with increasing chain length. Compounds with long chains (lauryl, cetyl) are completely inactive. The allyl compound is active but the β-bromoallyl derivative is less active and also toxic. NH_2 or acid residues in the side-chain destroy the activity almost or quite completely. *Thiazoloneimides*, CH—S / CH·NR > C:NH, are described in which R = Me, b.p. 96—98°/11 mm., m.p. 44—45° (*hydriodide*, m.p. 182—184°); *Et*, b.p. 100—103°/11 mm. (*hydriodide*, m.p. 110°, p-*toluenesulphonate*, m.p. 120—121°); *Pr*$^{\alpha}$, b.p. 105—108°/11 mm.; *Pr*$^{\beta}$, b.p. 106—108°/11 mm.; n-$C_{12}H_{25}$, a viscous oil; n-$C_{16}H_{33}$, a viscous oil; CH_2Ph (*hydrochloride*, m.p. 182—183°); ·$[CH_2]_2$·OH (*hydriodide*, m.p. 115°); ·CH_2·CO_2H, m.p. 255° (decomp.); ·CH_2·CO_2Et (*hydrochloride*, m.p. 195°); ·CH_2·CO·NEt_2 (*hydrochloride*, m.p. 193—194°); ·$[CH_2]_2$·NEt_2 (*dihydrochloride*, m.p. 243°). These compounds are converted by *p*-NO_2·C_6H_4·SO_2Cl preferably in presence of C_5H_5N or from 2-*p*-nitrobenzenesulphonamidothiazole by direct introduction of the requisite residue in aq. EtOH into 2-p-*nitrobenzenesulphonimidothiazolones*, CH—S / CH·NR > C:N·SO_2·C_6H_4·NO_2, in which R = *Me*, m.p. 209°; *Et*, m.p. 169—170°; *Pr*$^{\alpha}$, m.p. 195—197°; *Pr*$^{\beta}$, m.p. 163°; n-$C_{12}H_{25}$, m.p. 142·5—143°; n-$C_{16}H_{33}$, m.p. 131°; *allyl*, m.p. 145—146°; ·CH_2Ph, m.p. 210—211°; $[CH_2]_2$·NEt_2, m.p. 165°. The following 2-p-*aminobenzenesulphonamidothiazolones*, CH—S / CH·NR > C:N·SO_2·C_6H_4·NH_2, are described, the m.p. of their *Ac* derivatives being in parentheses: R = Me, m.p. 245—246° (270°); *Et*, m.p. 192—194° (192—194°); *Pr*$^{\alpha}$, m.p. 174° (178—180°); *Pr*$^{\beta}$, m.p. 175—177°; *Bu*$^{\alpha}$, m.p. 192—195° (213°); n-$C_{12}H_{25}$, m.p. 106°; n-$C_{16}H_{33}$, m.p. 106°; *allyl*, m.p. 165—166° (110—112°); ·CH_2·CBr:CH_2, m.p. 122—123° (205—207°); CH_2Ph, m.p. 185—187° (203—204°); ·$[CH_2]_2$·*OH*, m.p. 154—155° (230°); ·CH_2·CO_2H, m.p. 152—153° (222—223°); ·CH_2·CO·NEt_2, m.p. 232—233° (245—246°); ·$[CH_2]_2$·NEt_2, m.p. 147—148° (86—88°). 2-p-*Aminobenzenesulphonmethylamidothiazole* has m.p. 108—110°. H. W.

Thiazole sulphonamides.—See B., 1942, III, 115.

Structure-chemical investigations. Mills–Nixon effect with thiazole derivatives. H. Erlenmeyer and W. Schoenauer (*Helv. Chim. Acta*, 1941, **24**, 172—179E).—2-Chloro*cyclo*pentanone and $CS(NH_2)_2$ at 100° afford 2-*amino*cyclo*pentenothiazole hydrochloride* (decomp. >200°), converted by saturated K_2CO_3 into the free *base* (**I**), m.p. (anhyd.) 93—94° or (+1H_2O) m.p. 124—125°. Similar methods lead to 2-*amino*cyclo*hexenothiazole* (**II**), m.p. 87·5—88·5° [*hydrochloride*, m.p. 233—238° (decomp.)], 2-*amino*cyclo*heptenothiazole hydrochloride*, m.p. 204° (decomp.), and 2-*amino*cyclo*octenothiazole hydrochloride*, m.p. 186—188° (decomp.). (**I**) can be diazotised only with particular precautions; the product decomposes very readily with separation of an oil and couples with β-$C_{10}H_7$·OH to a dark red dye. The other thiazole derivatives can be diazotised without difficulty. Differences in the absorption spectra of the hydrochlorides of (**I**) and (**II**) in EtOH in the region 220—315 mμ. suggest a differing structure in the aminothiazole portion of the mol. in the fundamental or excited condition. (**I**) causes a persistent,





medium increase in blood pressure whereas the other compounds cause a diminution. It is suggested that (**I**) and (**II**) exist preferentially in the forms *A* and *B* respectively. H. W.

Reduction of benzoxazoles and benzthiazoles in liquid ammonia. C. M. Knowles and G. W. Watt (*J. Org. Chem.*, 1942, **7**, 56—62).—Benzoxazoles and benzthiazoles are reduced by Na in liquid NH_3 according to the scheme: C_6H_4<N / Z>CR + 2Na → [·Z·C_6H_4·N:CR]$_2$Na (**I**) where R = H or Ph and Z = O or S. When R = Cl the Na : thiazole ratio is increased from 2 to 4. Since the Na salts are unstable, the character of the products ultimately isolated depends on the treatment of the primary products. If the Na salts are neutralised by NH_4Br or are treated with EtBr, the corresponding Schiff bases are formed: (**I**) + 2NH_4Br → SH·C_6H_4·N:CH_2 + 2NaBr + 2NH_3 and (**I**) + 2EtBr → OEt·C_6H_4·N:CHEt + 2NaBr. If the salts or the Schiff's bases are placed under conditions favouring hydrolysis, the corresponding aminophenols or thiophenols are produced: OH·C_6H_4·N:CH_2 + H_2O → OH·C_6H_4·NH_2 + CH_2O and (**I**) + 2H_2O → SNa·C_6H_4·NH_2 + CH_2O + NaOH. That reduction by H_2 is more extensive than reduction by Na is shown by the isolation of a high yield of *o*-NHMe·C_6H_4·OH from the products of the reduction of benzoxazole by H_2. 2-Phenylbenzoxazole, m.p. 103°, is obtained in 80% yield by refluxing

(6 hr.) and finally distilling a mixture of NH_2Bz and *o*-NH_2·C_6H_4·OH. Considerable amounts of benzthiazole (**II**) are made by prolonged boiling of $NPhMe_2$ with S, distillation of the mixture, and purification of crude (**II**) through its nitrate. N-o-*Ethoxyphenylpropylideneimine*, b.p. 79—85°/1 mm., 200—205°/754 mm., the additive *compound*, o-NH_2·C_6H_4·*SH*,$Pb(OAc)_2$, m.p. >275°, and N-o-*thiolphenylmethylideneimine*, m.p. >120° (decomp.), appear new. M.p. are corr. H. W.

Thiazoles of anthraquinone series.—See B., 1942, II, 145.

Oxazolines.—See B., 1942, II, 129.

Cyanine dyes.—See B., 1942, II, 150.

Photographic sensitising dyes.—See B., 1942, II, 207.

VII.—ALKALOIDS.

New formula for chaksine. S. Siddiqui and Z. Ahmad (*J. Indian Chem. Soc.*, 1941, **18**, 589—590).—The new formula $C_{11}H_{21}O_3N_3$ for chaksine is challenged (cf. A., 1940, II, 383). W. C. J. R.

Erythrophleum **alkaloids. VI. Dehydrogenation of cassanic acid by selenium.** L. Ruzicka, G. Dalma, and W. E. Scott (*Helv. Chim. Acta*, 1941, **24**, 179—187E; cf. A., 1942, II, 121).—Dihydrocoumingine is converted by KOH–EtOH into ketohydroxycassanic acid (**I**), m.p. 253—255° (vac.), $[\alpha]_D^{20}$ +1°±1° in EtOH (*Me* ester, m.p. 121°, $[\alpha]_D^{20}$ +4°±1° in 95% EtOH, and its *Ac* derivative, m.p. 189°, and *oxime*, m.p. 210°), identical with the acid derived from cassaine. (**I**) is reduced by Na and EtOH to dihydroxycassanic acid, m.p. 262—265° (vac.), $[\alpha]_D^{20}$ −7°±1° in 0·1N-NaOH (Me ester, m.p. 172—174°, $[\alpha]_D^{20}$ +1°±1° in 95% EtOH). (**I**) is oxidised by CrO_3 in AcOH at 35—40° to diketocassanic acid (**II**), m.p. 225°, $[\alpha]_D^{20}$ −44°±1° in 95% EtOH (Me ester, m.p. 108°, $[\alpha]_D^{20}$ −46°±1° in 95% EtOH). (**II**) is reduced by Na amyloxide at 220° to *cassanic acid* (**III**), m.p. 224° (vac.), $[\alpha]_D^{20}$ +3°±2° in $CHCl_3$ (*Me* ester, m.p. 44°, $[\alpha]_D^{20}$ +4°±2° in 95% EtOH), mixed with a little *iso*cassanic acid (*Me* ester, m.p. 95°, $[\alpha]_D^{20}$ +10°±1° in 95% EtOH). Dehydrogenation of (**III**) by Se at 330—350° gives 1 : 7 : 8-trimethylphenanthrene, m.p. 144° [additive compound, m.p. 192—193°, with $C_6H_3(NO_2)_3$], thus proving that Todd's formula for the *Erythrophleum* alkaloids (cf. A., 1940, II, 198) is untenable. M.p. are corr. H. W.

Coumingidine, a new crystalline alkaloid from *Erythrophleum couminga*. E. Schlittler (*Helv. Chim. Acta*, 1941, **24**, 319—332E).—The bark is moistened with aq. NH_3 and extracted repeatedly with $C_2H_4Cl_2$. The first extracts contain mainly oily bases but the later extracts give *coumingidine* (**I**), probably $C_{26}H_{45}O_6N$ but possibly $C_{27}H_{43}O_6N$, m.p. 160—161° [*hydrochloride*, m.p. 217—219°; *Ac* derivative (**II**), m.p. 155°; *phenylthiocarbamate*, m.p. 146°], best purified through *nitrosocoumingidine*, (**III**), m.p. 174—174·5°, from which it is regenerated by CuCl in conc. HCl. (**I**) is hydrogenated (PtO_2 in AcOH) to *dihydrocoumingidine* (*Ac* derivative, m.p. 115—116·5°), isolated as the sparingly sol. *perchlorate*, m.p. 166—168°. Hydrolysis of (**I**) by 0·5N-H_2SO_4 gives monomethylaminoethanol identified as *methylaminoethyl* 3 : 5-*dinitrobenzoate*, m.p. 195—196·5°. Treatment of (**II**) or (**III**) with MeOH–K_2CO_3 leads to the *Me* ester, $C_{26}H_{40}O_6$ (**IV**), m.p. 204—206°. Treatment of the neutral product of the above hydrolysis with KOH–MeOH gives an acid, $C_{20}H_{30}O_4$, m.p. 209—211° (*Me* ester, m.p. 170—171°), not identical with *allo*cassaic acid. (**IV**) is hydrogenated (PtO_2 in AcOH) to a *substance*, $C_{26}H_{42}O_6$, m.p. 162°, hydrolysed to an acid, $C_{20}H_{32}O_4$, m.p. 232—234° (Me ester, m.p. 114°), which does not depress the m.p. of dihydrocassaic (ketohydroxycassanic) acid. Dehydrogenation (Se at 340°) of derivatives of (**I**) gives 1 : 7 : 8-trimethylphenanthrene. Alkaline fission of (**I**) gives poorer yields than that of coumingine or cassaine and treatment with aq. HCl or H_2SO_4 does not give a homogeneous product. With HCl in aq. EtOH (**I**) gives an unidentified *acid*, m.p. 205°, whilst with aq. $H_2C_2O_4$ it yields an *acid*, $C_{25}H_{36}O_5$, m.p. 173—173·5° (which absorbs 3 H_2 when hydrogenated), and cassaic acid. The aliphatic OH-acid has not been identified. H. W.

Erythroidine.—See B., 1942, III, 142.

VIII.—ORGANO-METALLIC COMPOUNDS.

Anhydrohydroxymercuri-5-chloro-2-hydroxydiphenyl.—See B., 1942, II, 182.

Existence of organo-metallic compounds of tantalum. B. N. Afanassiew (*Z. anorg. Chem.*, 1941, **245**, 381—382).—Slight evidence for the formation of very unstable organo-metallic compounds during the interaction of $TaCl_5$ with MgPhBr and MgEtBr has been obtained. C. R. H.

IX.—PROTEINS.

Recent advances in the chemistry of the proteins. D. C. Carpenter (*J. Chem. Educ.*, 1941, **18**, 274—276).—A brief summary. L. S. T.

Reversibility of heat-denaturation of proteins. M. L. Anson and A. E. Mirsky (*J. Physical Chem.*, 1942, **46**, 334—335).—Contrary to

the statement of Spiegel-Adolf and Henny (cf. A., 1941, II, 306) reversibility of heat-denaturation is not limited to scrum-albumin but has been demonstrated in hæmoglobin, trypsin, chymotrypsin, and pepsinogen. C. R. H.

Lability towards alkali of serine and threonine in proteins, and some of its consequences. B. H. Nicolet, L. A. Shinn, and L. J. Saidel (*J. Biol. Chem.*, 1942, **142**, 609—613).—Destruction of 30—50% and 14—33% of threonine and serine, respectively, is observed on refluxing whole silk (containing 0·23, 1·556, and 1·93 milliequiv. of threonine, serine, and total hydroxyamino-acids, respectively) with 0·1N-NaOH for 1 hr. in N_2. On acid hydrolysis, the formation of additional NH_3 beyond the normal "amide-NH_3," equiv. to the amount of hydroxyamino-acid destroyed which probably forms peptides of dehydroamino-acids, is observed. H. G. R.

Threonine, serine, cystine, and methionine content of peanut proteins. W. L. Brown (*J. Biol. Chem.*, 1942, **142**, 299—301).—Arachin and conarachin contain respectively 2·56 and 2·02% of threonine, 5·2 and 4·99% of serine, 0·4 and 0·78% of cystine-S, and 0·14 and 0·45% of methionine-S. R. L. E.

Denaturation of proteins and its apparent reversal. I. Horse serum-albumin. II. Horse serum-pseudoglobulin.—See A., 1942, III, 416.

Effect of conditions of hydrolysis and of prolonged heating on the optical rotation of sulphuric acid hydrolysates of zein. R. Borchers and C. P. Berg (*J. Biol. Chem.*, 1942, **142**, 693—696).—Appreciable racemisation or destruction of NH_2-acids does not occur during the course of the hydrolysis of zein with aq. H_2SO_4 (14—33 vol.-%) either under a reflux condenser or in an autoclave at 120—180°. Prolonging the refluxing to 36 to 60 hr. has little or no effect but autoclaving longer than necessary for hydrolysis induces both racemisation and destruction, more markedly so at the higher temp. Concns. of H_2SO_4 as low as 8 vol.-% are not suitable for the complete and uncomplicated hydrolysis of zein. H. W.

Factors which influence oxidation of thiol groups.—See A., 1942, II, 189.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Isolation, properties, and constitution of flax pectin and its cleavage products.—See A., 1942, II, 187.

Structure of biotin. V. du Vigneaud, K. Hofmann, and D. B. Melville (*J. Amer. Chem. Soc.*, 1942, **64**, 188—189).—Curtius degradation of biotin Me ester gives *biotin hydrazide*, $C_{10}H_{18}O_2N_4S$, m.p. 238—240°, and thence the *Et urethane*, m.p. 188—190°, hydrolysed with loss of CO_2 by $Ba(OH)_2$ at 140° to a triamine, $C_8H_{19}N_3S$ (*Bz*$_3$ derivative, m.p. 194—195°), whence no adipic acid could be obtained (cf. A., 1942, II, 131). Various structures for biotin are discussed. R. S. C.

Active principles of leguminous fish-poison plants. VI. Robustic acid. S. H. Harper (*J.C.S.*, 1942, 181—182).—From the ethereal extract of *Derris robusta* there has been isolated *robustic acid*, $C_{27}H_{24}O_8$ (less probably $C_{28}H_{26}O_8$), m.p. 190°, which is monocarboxylic, contains two OMe, gives a *K* salt and *Me* ester, m.p. 190°, and is reduced (PtO_2–H_2 in EtOAc) to the H_2-acid, m.p. 180° (*Me* ester, m.p. 207—208°). The acid is probably related to lonchocarpic acid as it gives the same sequence of colour changes in the Durham test. F. R. S.

XI.—ANALYSIS.

Adsorption analysis.—See A., 1942, I, 211.

Micro-Kjeldahl determination of nitrogen. A new indicator and an improved rapid method. T. S. Ma and G. Zuazaga (*Ind. Eng. Chem. [Anal.]*, 1942, **14**, 280—282).—The sample is digested with H_2SO_4 in the presence of Se, $CuSO_4$, and K_2SO_4. NH_3 is distilled into 2% H_3BO_3 solution and titrated directly with 0·01N-HCl, using a mixed (1 : 5) indicator of Me-red–bromocresol-green. The digestion usually takes ~10 min. Apparatus is described in detail; manipulation is easy and accuracy good. J. D. R.

Micro-determination of chlorine in volatile organic compounds. A. F. Colson (*Analyst*, 1942, **67**, 47—51).—Methods of Pregl and of Elek and Hill (A., 1933, 843) give low results for the Cl content of volatile substances such as CCl_4. The vapour of the org. compound mixed with O_2 is passed over heated Pt and CaO in succession. A column of cold, fused Na_2CO_3 serves to trap any Cl_2 escaping from the heated CaO. After dissolution of the CaO in HNO_3 the Cl is pptd. with $AgNO_3$. Using CCl_4 errors of ±0·4% were obtained. S. B.

Improved methoxyl apparatus. A. J. Bailey (*Ind. Eng. Chem. [Anal.]*, 1942, **14**, 181).—The apparatus embodies a water-jacketed electrically-heated column (internal heater) and a modified absorption system. It may be used in the Zeisel or Vieböck method (absorption in Br–KOAc–AcOH). J. D. R.

Determination of volatile fatty acids. F. Hillig and L. F. Knudsen (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 176—195).—A steam-distillation procedure is given. If a single, known, volatile acid is present the 50- and 200-ml. portions of distillate are titrated separately, blanks being deducted, and the quantity of acid is computed by reference to a table of distillation rates. This table may also be used to identify the acid. For two-acid systems the results are calc. by means of simultaneous equations involving distillation rates of the separate acids. Analogous equations are given for three-acid systems (HCO_2H being absent) and four-acid systems (HCO_2H being present). A tabular method for solving simultaneous equations is appended. A. A. E.

Alkalimetric determination of amines. B. P. Fedorov and A. A. Spriskov (*Prom. Org. Chim.*, 1936, **1**, 620).—0·3 g. of the aromatic amine is dissolved in 2—15 c.c. of Et_2O, and 1—2 c.c. of dry Et_2O saturated with HCl are added. The mixture is evaporated at room temp. or at 30—40°; the residue is dried at 40—50° (15—20 min.), and dissolved in 100 c.c. of H_2O. 80% of the required vol. of 0·1N-NaOH is added, and the titration completed in hot solution, with phenolphthalein as indicator. C_6H_6 may be used instead of Et_2O. Poor results are obtained in the determination of *p*-$NH_2{\cdot}C_6H_4{\cdot}OH$ (solution coloured), quinoline, C_5H_5N, 1-amino-anthraquinone (low solubility in Et_2O), and $NPhMe_2$ (low basicity). CH. ABS. (*w*)

Micro-technique of organic qualitative analysis. Identification of compounds containing nitrogen. C. R. García and F. Schneider (*Ind. Eng. Chem. [Anal.]*, 1942, **14**, 94—97).—The substances are classified by micro-titration as acidic, basic, or neutral. In the acidic class, Millon's test, Mulder's reaction, the murexide reaction, and the Adamkiewicz–Hopkins–Cole reaction are detailed. In the basic class, sp. tests are described for NH_3, NH_4 salts, and primary amines, by treatment with HNO_2, and the Rimini test for primary and the Simon test for *sec.* aliphatic amines are detailed. Procedure is given for the acetylation and benzoylation of 3—6 mg. of amines, for the prep. of picramides, picrates, arylsulphonyl derivatives, and salts of amines with 2 : 5 : 1-$(NO_2)_2C_6H_3{\cdot}CO_2H$ and *p*-$C_6H_4Me{\cdot}SO_3H$. In the neutral class, a sp. test for the NO_2-group is given, and procedures are detailed for the acid and alkaline hydrolysis of N compounds. J. D. R.

Determination of *d*-amino-acids.—See A., 1942, III, 503.

Aromatic sulphonic acids as reagents for amino-acids. Preparation of *l*-serine, *l*-alanine, *l*-phenylalanine, and *l*-leucine from protein hydrolysates.—See A., 1942, II, 189.

Qualitative test for ethylene- and propylene-thiocarbamides. C. O. Edens and T. B. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 3527).—2-Thiotetrahydroglyoxaline (~0·001M.) or its 4-Me derivative with 1 : 1 saturated aq. $CuSO_4$–conc. HCl gives in a spot test a gelatinous ppt. of fibre-like crystals. R. S. C.

Substituted semicarbazones. III. Attempted application to the determination of glucose. G. H. Baril, R. Barré, and L. Piché (*Canad. J. Res.*, 1942, **20, B**, 33—39; cf. A., 1942, II, 169).—Formation of glucose-δ-*p*-nitrophenylsemicarbazone (**I**) in aq. EtOH increases from ~30 to ~80% as the $[H_2O]$ is decreased from 75 to 6% and becomes quant. if $C_5H_{11}{\cdot}OH$ is added and the solution is evaporated to remove all H_2O. Approx. the correct amount (determined by a trial run) of *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2$ (**II**) is used; the excess of (**II**) is removed by adding *m*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ and removing its insol. *p*-nitrophenylsemicarbazone (**III**); warming the filtrate after addition of dil. HCl then hydrolyses the sol. (**I**), yielding a corresponding amount of (**III**), which is collected and weighed. Results are approx. correct but the method is not considered final. R. S. C.

Bromometric determination of hydroxybenzenes. W. Bielenberg, H. Goldhahn, and A. Zoff (*Oel u. Kohle*, 1941, **37**, 496—500).—Koppeschaar's method for determining PhOH (addition of excess of KBr–$KBrO_3$, followed after 15 min. by addition of KI and titration of excess of Br with $Na_2S_2O_3$), is inaccurate when applied to other hydroxybenzenes. A direct bromometric method for determining hydroxybenzenes has been evolved. 25 c.c. of a 0·2% aq. solution of the material are shaken with an excess of 0·1N-KBr–$KBrO_3$ and the excess of Br is back-titrated with 0·1N-As_2O_3 or 0·01N-$Na_2S_2O_3$. Data showing the effects of the period of shaking and the time elapsing before back-titration on the accuracy of the results obtained with PhOH, *o*-, *m*-, and *p*-cresol, *m*- and *p*-$C_6H_4(OH)_2$, and phloroglucinol are tabulated. The direct bromometric method gives higher vals. than the Koppeschaar method except in the cases of PhOH and *m*-cresol, when both methods yield the same results. The causes for these phenomena are being studied. R. B. C.

Volumetric determination of uric acid. Y. V. Narayanayya (*Current Sci.*, 1941, **10**, 405—406).—$Ce(SO_4)_2$ is used instead of $KMnO_4$ in the usual titrimetric method, because it can be used in presence of high concn. of Cl′ and an exceedingly sharp end-point is obtained with *o*-phenanthroline–Fe^{II} complex indicator. The method is described. J. N. A.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JULY, 1942.

I.—ALIPHATIC.

Recent methods used in preparative organic chemistry. IX. Substitution in aliphatic compounds. J. Nelles (*Angew. Chem.*, 1941, **54**, 77—85).—A literature survey. A. T. P.

Identification of homologous organic compounds or isomerides by their near infra-red absorption spectra.—See A., 1942, I, 193.

New methods of preparative organic chemistry. XHI. Hydrogenation with Raney catalysts. R. Schröter (*Angew. Chem.*, 1941, **54**, 229—234).—The prep. and uses of the catalysts are discussed. H. W.

Zinc–nickel couple in the hydrogenation of organic compounds. V. Harlay (*Compt. rend.*, 1941, **213**, 304—305).—Zn–Ni couple, produced by immersing Zn in an ammoniacal solution of a Ni salt, has been used successfully in reducing galactose to dulcitol and fructose to mannitol in neutral solution. In the presence of NH_3 or alkali hydroxides it has also been used for reducing ethylenic compounds, aldehydes, ketones, ketonic acids, oximes, $CH_2Ph{\cdot}CN$, and *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$. Ketones can be converted directly into amines by reduction with Zn–Ni in aq. NH_3–EtOH solution. J. W. S.

Catalytic isomerisation of normal paraffins.—See B., 1942, II, 177.

Isomerisation of hydrocarbons.—See B., 1942, II, 177.

Alkylation of hydrocarbons.—See B., 1942, II, 138.

Catalytic dimerisation of ethylene. S. J. Pscheshetzki (*J. Phys. Chem. Russ.*, 1940, **14**, 1376—1377).—Ni containing 1% of unspecified metal oxides transforms C_2H_4 into butylene and smaller amounts of other hydrocarbons. The catalyst can be regenerated by an air current at 700°; 2 min. of regeneration are required after 1 hr. of use. J. J. B.

Polymerisation of olefines.—See B., 1942, II, 138.

Production of olefine dimerides.—See B., 1942, II, 138.

Dehydrogenation of open-chain hydrocarbons in presence of carbon dioxide. A. A. Balandin (*J. Phys. Chem. Russ.*, 1940, **14**, 1378—1379).—Activated Cr_2O_3 catalysts produce from C_4H_{10} and CO_2 CH_4, CO, and H_2; from PhEt and CO_2 chiefly styrene (at 650°); and from butylene and CO_2 chiefly butadiene. J. J. B.

Catalytic dehydrogenation of butane. G. D. Liubarski (*J. Phys. Chem. Russ.*, 1940, **14**, 1375).—When 1500 l. of C_4H_{10} are passed through 1 l. of $Cr_2O_3 + Al_2O_3$ (or of $V_2O_5 + Al_2O_3$) per hr. at 525—575° and atm. pressure, 600 l. of C_4H_8 are formed and 120—220 l. of C_4H_{10} are used for other reactions. C deposited on the catalyst is periodically burnt out in an air current. J. J. B.

Polymerisation of $\Delta^{\alpha\gamma}$-butadienes.—See B., 1942, II, 138.

Partial reduction of acetylenes to olefines using an iron catalyst. II. Reduction of eninenes and dieninenes. A. F. Thompson, jun., and E. N. Shaw (*J. Amer. Chem. Soc.*, 1942, **64**, 363—366).—Hydrogenation of C:C in presence of the Fe catalyst from Fe–Al (A., 1940, II, 362) ceases at CH:CH only in the case of CR:CR′ (except for tolane). In other cases hydrogenation of C:C then occurs, but more slowly, so that here too the olefines are readily isolated. The C:C·C:C stage is also obtained from C:C·C:C. Examples are the hydrogenation at 100°/1000 lb. of CH:C·CPr$^{\beta}_2$·OH, CH:C·CMe:CH_2, CH:C·CEt:CHMe (I), b.p. 96·5°, CH:C·CPr$^{\alpha}$:CHEt (**II**), b.p. 136—137°, and CBu$^{\alpha}$:C·CMe:CHR (R = Me, Et, or Bu$^{\alpha}$). The nature of the products is proved by absorption of 2 H_2 in presence of PtO_2 and, for CHBu$^{\alpha}$:CH·CMe:CHR, by the exaltation of *n* and formation of amorphous products by addition of (:CH·CO)$_2$O. (:C·CMe:CH_2)$_2$ and di-Δ^1-*cyclo*hexenylacetylene are reduced only at 130°/1700 lb. (only 1 H_2 absorbed) and give products considered to be allenes (CMe_2:C:CH·CMe:CH_2 and α-Δ^1-*cyclo*hexenyl-β-*cyclo*hexylideneethylene) because of their stability and normal *n*. (**I**) and (**II**) are obtained in 50—60% yield by adding CH:C·CRR′·OH to boiling 5% *p*-$C_6H_4Me{\cdot}SO_3H$–Ac_2O. CHBu$^{\alpha}$:CH·CMe:CHR, in which R = Me, b.p. 38—40°, Et, b.p. 48—50°, and Bu$^{\alpha}$, b.p. 74—75°, and described. CBu$^{\alpha}$:C·CMe:CHR are obtained by condensing CBu$^{\alpha}$:C·MgBr with COMe·CH_2R and dehydrating the resulting carbinol by Al_2O_3 at 230°. R. S. C.

Catalytic hydrogenation and polymerisation of acetylene–hydrogen mixtures. Synthesis of *iso*butene from acetylene and hydrogen. A. D. Petrov and L. I. Antzus (*J. Phys. Chem. Russ.*, 1940, **14**, 1308—1312).—NiO deposited on >20 parts of pumice transforms at 160—180° C_2H_2–H_2 mixtures into 60% of liquid, 10% of tar, and 30% of heavier gas; the yield of liquid of b.p. <160° is 60% when the hydrogenation takes place at 1 atm. or 70% at 20 atm. If the catalyst contains also $ZnCl_2$ or H_3PO_4 the I val. of the liquid reaction product is higher. H_3PO_4 raises the yield of liquid of high b.p. $ZnCl_2$ (5 parts for 1 part of Ni) raises the yield of gas to 70—80%; 0·9 of the gas is *iso*butene, the rest is divinyl and C_2 hydrocarbons. The liquid contains more even hydrocarbons (C_4, C_6, C_8, C_{10}) than odd ones. J. J. B.

Correlation of molecular structure of halogeno-hydrocarbons with their b.p.—See A., 1942, I, 232.

Manufacture of halogenated hydrocarbons.—See B., 1942, II, 138.

Brucine as a reagent for partly resolving bromoalkanes. Configurations of diasteroisomeric dibromoalkanes. H. J. Lucas and C. W. Gould, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 601—603).—Partial resolution by brucine (by differing rates of formation of quaternary salts; cf. A., 1942, II, 72) confirms previous allocations of configuration. Resolutions are effected as follows: *dl*-(CHMeBr)$_2$ → α_D^{25} −2·04°; *dl*-(CHEtBr)$_2$ → α_D^{25} +0·07°; *dl*-(CHPr$^{\alpha}$Br)$_2$ → α_D^{25} +0·14°. The corresponding *meso*-compounds were not resolvable [except that 97% pure *meso*-(CHMeBr)$_2$ → α_D^{25} −0·07°]. Impure, commercial CHMeBr·CH_2Br gave samples having α_D^{25} +0·30°, +0·65°, and +0·81° (twice), and a cryst., quarternary *salt* was isolated. R. S. C.

Halogen addition to ethylene derivatives. I—III.—See A., 1942, I, 243.

Preparation of pentaerythritol.—See B., 1942, II, 179.

Nitro-alcohols.—See B., 1942, II, 178.

Reaction of epichlorohydrin with the Grignard reagent. J. K. Magrane, jun., and D. L. Cottle (*J. Amer. Chem. Soc.*, 1942, **64**, 484—487).—Mg[CH(CH_2Br)·CH_2Cl]$_2$ (**I**), prepared from epichlorohydrin (**II**) by $MgBr_2$–Et_2O or from $CH_2Br{\cdot}CH(OH){\cdot}CH_2Cl$ (**III**) by MgEtBr, with MgEtBr gives, in amounts varying according to the conditions, C_2H_4, C_2H_6, (**III**), and *cyclo*propanol (**IV**), b.p. 101—103° [formed from (**III**)], and tar. The structure of (**IV**) follows from its yielding a *phenyl*-, m.p. 102°, and *α-naphthyl-urethane*, m.p. 101—102°, and 3 : 5-*dinitrobenzoate*, m.p. 109°, and its conversion by alkali into resins, by hot HCO_2H into an aldehyde, and by repeated distillation into EtCHO, but attempts to convert it into other substances failed. $CH_2Cl{\cdot}CHPr^{\alpha}{\cdot}OH$ (**V**) and MgEtBr in Et_2O at room temp. give slowly $CHPr^{\alpha}_2{\cdot}OH$. MgEtBr and (**II**) give (**III**), (**IV**), (**V**), and tar in amounts varying according to the conditions. 70—83% of (**IV**) is obtained from (**II**) by 0·5 mol. of $MgEt_2$. Interaction of (**II**) and MgEtBr proceeds by way of (**I**). R. S. C.

Production of ethylene oxide.—See B., 1942, II, 179.

Acetylenic ethers. II. Ethoxy- and butoxy-acetylene. T. L. Jacobs, R. Cramer, and J. R. Hanson (*J. Amer. Chem. Soc.*, 1942, **64**, 223—226; cf. A., 1940, II, 305).—$CH_2Br{\cdot}CHBr{\cdot}OBu$ and Na–BuOH at 70—80° give *Bu$_2$ bromoacetal* (89%), b.p. 139—140°/33 mm., 86·5°/1 mm., and thence by Br *Bu$_2$ dibromoacetal* (**I**) (40—50%), b.p. 104°/1 mm., $CH_2Br{\cdot}CO_2Bu$, and BuBr. Addition of Zn dust (activated by 3N-HCl) (2 mols.) to $CHBr_2{\cdot}CH(OEt)_2$ in boiling 95% EtOH gives *α-bromo-β-ethoxyethylene* (50%), b.p. 41—44°/19 mm., which with KOH (2 pts.) at 90—100° gives *ethoxyacetylene* (**II**) (50—55%), b.p. 27·5—28·5°/300 mm. Zn in EtOH reacts more slowly with (**I**), giving *α-bromo-β-butoxyethylene* (**III**) (usually 55—78%), b.p. 60°/8 mm., and *Et Bu bromoacetal* (6—65%), b.p. 95—96°/4 mm. Distillation of (**III**) with KOH at 370 mm. gives 34—56% of *butoxyacetylene* (**IV**), b.p. 50·5°/110 mm. (**II**) and (**IV**) give impure black Ag derivatives, which (fresh) in dil. H_2SO_4 or HNO_3 give a little ROAc. (**II**) gives an unstable white Hg derivative and consumes 1 mol. of MgMeI to give CH_4. (**II**) and (**IV**) are stable only at −80° (sealed tube) and at ~100° (sealed tube) explode. Hydrogenation (2 H_2; PtO_2) of (**IV**) in EtOH is rapid, yielding EtOBu and EtOH (azeotrope, b.p. 73—74°, containing 59 mol.-% of EtOH), but, in presence of Pt or Pd, (**II**) absorbs only 1 H_2 readily and a second mol. slowly and incompletely (Et_2O isolated). 0·05M-Acid hydrolyses (**II**) very rapidly to EtOAc. Acid hydrolysis of (**IV**) is also rapid and

boiling H_2O gives BuOAc (67%) and polymerides. Hydrolysis of (IV) by H_2O at room temp. is slow. Boiling EtOH has no effect on (II), but with BF_3–EtOH–HgO at 0° (II) gives Et_2O (47%) and EtOAc (50%), probably by way of $CH_2{:}C(OEt)_2$ and $CMe(OAc)_3$ [$CMe(OAc)_3$ gives the same products]. The reactivity in additive reactions is $CH_2{:}CH{\cdot}OEt < CH{:}C{\cdot}OEt < CH_2{:}C(OEt)_2$. (II) is anæsthetic but poisonous (mice). $CH{:}C{\cdot}OPh$ is poisonous and not anæsthetic. R. S. C.

Production of ethers of polyhydric alcohols.—See B., 1942, II, 140.

Manufacture of methyl borate.—See B., 1942, II, 139.

Alkyl nitrites. VII. Synthesis of organic nitrites and nitrates. S. E. Forman, C. J. Carr, and J. C. Krantz, jun. (*J. Amer. Pharm. Assoc.*, 1941, **30**, 132—133).—The following were prepared from the alcohols and acids: *β-ethyl*-n-*hexyl*, b.p. 63°/19 mm., and n-*octadecyl nitrite*, b.p. 138—144°/1 mm., *iso*amyl lactate, b.p. 96—100°/23 mm., Pr, b.p. 74—75°/21 mm. (*nitrate*, b.p. 94—96°/19 mm.), *Bu*, b.p. 87—88°/20·5 mm. (*nitrate*, b.p. 109·5—110°/19—19·5 mm.), and *heptyl glycollate*, b.p. 125—130°/16—17 mm., and iso*mannide*, m.p. 65·5°, iso*sorbide*, m.p. 52°, and *erythritan dinitrate*, b.p. 89°/1 mm. The following were also prepared (impure): *n*-nonyl, b.p. 63°/2 mm., *α*-methyl-δ-ethyl-*n*-octyl, b.p. 67°/2 mm., lauryl, b.p. 90°/2 mm., *η*-ethyl-*β*-methyl-*n*-hendecyl δ-, b.p. 87°/2 mm., myristyl, b.p. 110°/1 mm., and cetyl nitrite, heptyl glycollate, b.p. 146°/17 mm., glyceryl *αγ*-diacetate *β*- and inositol nitrate, adonitol pentanitrate, and polygalitol and sorbitan tetranitrate. (For pharmacological properties of some of these compounds, see A., 1939, III, 85; 1940, III, 62, 333; 1941, III, 216.) F. O. H.

Alkyl esters of phosphoric acid.—See B., 1942, II, 137.

Use of phenylhydrazine to characterise organic acids. G. H. Stempel, jun., and G. S. Schaffel (*J. Amer. Chem. Soc.*, 1942, **64**, 470—471).—When acids and $NHPh{\cdot}NH_2$ are, usually, boiled alone or in C_6H_6, good yields of phenylhydrazides or, from strong acids, salts are obtained. The following are recorded. Form-, m.p. 143° (lit. 145°), *n*-butyr-, m.p. 102° (lit. 103°), *n*-hexo-, m.p. 98° (lit. 96·5°), *n*-octo-, m.p. 106° (lit. 104°), lact-, m.p. 115° (lit. 114·5°), n-*valer*-, m.p. 109°, n-*deco*-, m.p. 105°, n-*undeco*-, m.p. 110°, *α-ethyl*-n-*butyr*-, m.p. 145°, and *undeceno*-, m.p. 97°, *-phenylhydrazide*; adip-, m.p. 209° (lit. 207°), succin-, m.p. 210° (lit. 209°), *sebac*-, m.p. 194°, and *malon*-, m.p. 194°, *-bisphenylhydrazide*; *NHPh·NH₂ chloro*-, m.p. 111°, and *trichloro-acetate*, m.p. 123°, *α-chloropropionate*, m.p. 95°, *benzene*-, m.p. 179°, and p-*toluene-sulphonate*, m.p. 188°. R. S. C.

Photolysis of methyl acetate.—See A., 1942, I, 245.

Determination of esterification constants in presence of a neutral solvent. H. Gault and A. Chablay (*Compt. rend.*, 1941, **213**, 177—179).—The effects of H_2O formed in the reaction $C_nH_{2n+1}{\cdot}CO_2H + MeOH \rightleftharpoons C_nH_{2n+1}{\cdot}CO_2Me + H_2O$ may be obviated by employing equimol. proportions of the reactants at 175° in dioxan to maintain a homogeneous system. No variation of the esterification const. is found for acids with $n = 1, 2, 3, 4, 5, 6, 7, 15$. C. S.

[Preparation of] highly-branched brominated organic acids and esters.—See B., 1942, II, 179.

Condensation of chloral with ethyl acetoacetate. D. R. Kulkarni and N. M. Shah (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 120—121).—*Et α-β′β′β′-trichloro-α′-hydroxyethylacetoacetate* (*acetate*, b.p. 120°/7 mm.), is obtained when a mixture of $CH_2Ac{\cdot}CO_2Et$ (1 mol.), freshly distilled $CCl_3{\cdot}CHO$ (1·2 mols.), and C_5H_5N (1 c.c. per 11 g. of mixture) is kept at 25—30° for 5 days. Its constitution follows from its conversion by *m*-$C_6H_4(OH)_2$ into 7-hydroxy-4-methyl-3-*βββ*-trichloro-*α*-hydroxyethylcoumarin. H. W.

Introduction of the *tert.*-butyl group into ethyl acetoacetate by means of boron trifluoride. C. R. Hauser and J. T. Adams (*J. Amer. Chem. Soc.*, 1942, **64**, 728).—$CH_2Ac{\cdot}CO_2Et$ (1), $Bu^{\gamma}OH$ (1 mol.), and BF_3 at room temp. give *Bu*$^{\gamma}$ *α*-tert.-*butylacetoacetate* (14%), b.p. 101—102°/20 mm. (cf. A., 1940, II, 374). R. S. C.

Carboxylation. I. Photo-chemical and peroxide-catalysed reactions of oxalyl chloride with paraffin hydrocarbons. M. S. Kharasch and H. C. Brown. **II. Reaction of oxalyl chloride with unsaturated hydrocarbons.** M. S. Kharasch, S. S. Kane, and H. C. Brown (*J. Amer. Chem. Soc.*, 1942, **64**, 329—333, 333—334).—I. $(COCl)_2$ and saturated hydrocarbons do not react in the dark in absence of peroxides. In light, *cyclo*-hexane and -pentane, methyl-*cyclo*-hexane and -pentane, chloro*cyclo*hexane, *n*-C_5H_{12}, *n*-C_7H_{16}, and *iso*octane give the derived acid chlorides, RCOCl. The reaction mechanism is: $(COCl)_2 \rightarrow 2COCl$ and/or $CO{\cdot}COCl + Cl$; $COCl \rightarrow CO + Cl$; $CO{\cdot}COCl \rightarrow 2CO + Cl$; $RH + Cl \rightarrow R + HCl$; $R + (COCl)_2 \rightarrow RCOCl + COCl$, etc. The chain is of moderate length. Yields are lowered by formation of coloured light-absorbing impurities. Diluents, *e.g.*, CCl_4, slow the reaction, but C_6H_6 etc. inhibit it (? by absorption of light). RCO·COCl is not formed because (i) $AcCO_2H$ and $(COCl)_2$ in C_6H_6 give only ? $[{\cdot}CO_2C({:}CH_2){\cdot}COCl]_2$, (ii) $BzCO_2H$ and $(COCl)_2$ at the b.p. give BzCOCl (75%), and (iii) decomp. of Bz_2O_2 in $(COCl)_2$ gives BzCl (70%), but not BzCOCl or PhCl. Bz_2O_2 catalyses interaction of $(COCl)_2$ and *cyclo*hexane in the dark (by formation of R·), yielding 65% of *cyclo*hexanecarboxyl chloride; chloro*cyclo*hexane and *n*-C_7H_{16} give 60 and 50% yields, respectively, of RCOCl; the chain length is short since 5% of Bz_2O_2 is needed for good yields.

II. Interaction of $(COCl)_2$ with unsaturated compounds is not catalysed by light or peroxides; only highly polar compounds react and the mechanism is polar. $(COCl)_2$ with $CH_2{:}CPh_2$, $CH_2{:}CHPh$, $CH_2{:}CPhMe$, and 1-methyl*cyclo*hexene at the b.p. gives $CPh_2{:}CH{\cdot}COCl$ (50%), $CHPh{:}CH{\cdot}COCl$ (9%), $CPhMe{:}CH{\cdot}COCl$, and 1-methyl*cyclo*hexenecarboxyl chloride (6%), respectively; with $CH{:}CPh$ it gives $CPhCl{:}CH{\cdot}COCl$ (16%). *cyclo*Hexene, $CHMe{:}CMe_2$, $(CHPh)_2$, *n*-$C_{16}H_{32}$, C_8H_{16}, and $(CHCl)_2$ do not react. R. S. C.

Mixed electrolytes of nitrates with adipates, lævulates, and *β-iso*-amyloxypropionates. F. Fichter and J. Herndl (*Helv. Chem. Acta*, 1942, **25**, 229—240).—Electrolysis of solutions containing NO_3' and adipate yields the dinitrates of *butane-αβ-diol*, b.p. 114—115°/11 mm., butane-*αβδ*- (I) and -*αβγ*-triol, and erythritol. These nitrates result from $CH_2{:}CHEt$, the normal product of the electrolysis of adipic acid (II), which is hydroxylated at the anode to butane-*αβ*-diol and then immediately converted into the corresponding nitrate. The oxidising action of the Pt anode in an electrolyte containing NO_3' causes the introduction of a further one or two OH; $(CH_2{\cdot}O{\cdot}NO_2)_2$, which is also obtained, is derived from $(CH_2{\cdot}CO_2H)_2$ arising from the oxidation of (II). Electrolysis of solutions of NO_3' and lævulate does not yield products characteristic for $Ac{\cdot}[CH_2]_2{\cdot}CO_2H$ but exclusively substances derived from $(CH_2{\cdot}CO_2H)_2$, viz., $(CH_2{\cdot}O{\cdot}NO_2)_2$ and $([CH_2]_2{\cdot}O{\cdot}NO_2)_2$. The electrolytic oxidation of $Ac{\cdot}[CH_2]_2{\cdot}CO_2H$ to $(CH_2{\cdot}CO_2H)_2$ is readily understandable since it is purely chemically oxidised to $(CH_2{\cdot}CO_2H)_2$ by HNO_3; in addition to these compounds obtained from succinate–NO_3', (I) is also obtained as a consequence of the increased oxidising power of the anode due to higher c.d. and higher $[NO_3']$. Electrolysis of NO_3'–*iso*amyloxypropionic acid gives *iso*-$C_5H_{11}{\cdot}OH$, *iso*amyl *β-iso*amyloxypropionate, and a nitrate of butane-*αβδ*-triol di*iso*amyl ether which could not be obtained pure. The following appear new: *butane-αβδ-triol dicarbanilide*, m.p. 132°; *butane-αβγ-triol tricarbanilide*, m.p. 135—136°; *erythritol dinitrate*, m.p. 84·5—85° (explosive). H. W.

Forms of calcium tartrate derived from *d*-tartaric acid. (Mlle.) T. Pobeguin (*Compt. rend.*, 1941, **213**, 203—206).—*d*-Tartaric acid and $Ca(OAc)_2$ (slight excess) at room temp. afford an unstable form of the Ca salt (+$6H_2O$) (cf. Chattaway, A., 1917, i, 4) (also obtained from *Zebrina pendula*, Comm.), readily convertible into the orthorhombic, more stable form (+$4H_2O$). A. T. P.

Depolymerisation of aconitic acid: $(CH{\cdot}CO_2H)_3$. I. D. S. Rao (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 56—68).—In the thermal decomp. of aconitic acid (I) appreciable amounts of fumaric acid (II) and C_2H_4 are formed. It is suggested that (I) behaves as a trimeride of the labile radical $CH{\cdot}CO_2H$ (III), and that the mechanism of decomp. is (1) $(CH{\cdot}CO_2H)_3 = (II) + (III)$; (2) $(III) = CH_2 + CO_2$; (3) $2CH_2 = C_2H_4$; (4) $CH_2 + (II) =$ itaconic acid. (I) is quantitatively transformed into (II) when the aq. solution is shaken with active C. F. J. G.

Manufacture of organic sulphur compounds [esters of *β*-thiol-aliphatic acids.—See B., 1942, II, 180.

Production of hydroxycitronellal.—See B., 1942, II, 180.

Purification of ketones.—See B., 1942, II, 141.

Manufacture of methylketen and propionic anhydride.—See B., 1942, II, 181.

Keten acetals. VII. Reaction of keten diethyl acetal with halogen compounds and acids. S. M. McElvain and D. Kundiger (*J. Amer. Chem. Soc.*, 1942, **64**, 254—259; cf. A., 1940, II, 296).—$CH_2{:}C(OEt)_2$ (I) (0·23) and $Bu^{\alpha}Br$ (0·45 mol.) at 250° (72 hr.) give 13% of *n*-$C_5H_{11}{\cdot}CO_2Et$ [by way of *n*-$C_5H_{11}{\cdot}CBr(OEt)_2$] and EtBr (20%), but simultaneous decomp. leads to much EtOAc and C_2H_4. This decomp. does not occur with the more reactive $CH_2{:}CH{\cdot}CH_2Br$ and CH_2PhBr (46% reaction at 190° in 5 hr. and 71% at 125° in 3 hr., respectively), but much dialkylation also occurs; reactions are: (I) + RBr → $[CH_2R{\cdot}CBr(OEt)_2]$ (II) → $CH_2R{\cdot}CO_2Et$ + EtBr; (II) → $[CHR{:}C(OEt)_2]$ (III) + HBr; (II) + HBr → EtOAc + EtBr; (III) + RBr → $[CHR_2{\cdot}CBr(OEt)_2] \rightarrow CHR_2{\cdot}CO_2Et$ + EtBr; (III) + EtOH [obtained by decomp. of (I)] → $CH_2R{\cdot}C(OEt)_3$. Addition of AcCl (1) to (I) (1 mol.) at 55° causes the reactions: (*a*) (I) + AcCl → EtCl + $CH_2Ac{\cdot}CO_2Et$ (3% isolated) → (+AcCl) $OAc{\cdot}CMe{:}CH{\cdot}CO_2Et$ (IV) (30%) + HCl; (*b*) (I) + HCl → EtOAc + EtCl; (*c*) 2(I) + HCl → $[(OEt)_2CMe{\cdot}CH_2{\cdot}CCl(OEt)_2] \rightarrow OEt{\cdot}CMe{:}CH{\cdot}CO_2Et$ (V) (26%) + EtCl + EtOH. The yield of (IV) is 52% if 3 mols. of AcCl are used. The validity of (*a*) is proved by formation of 79% of (IV) + $CHAc_2{\cdot}CO_2Et$ when $CH_2Ac{\cdot}CO_2Et$ is treated with AcCl + (I), the (I) functioning by removal of HCl. BzCl reacts more sluggishly but similarly with (I) at 100°, except that (*c*) does not occur. *Et O-benzoylbenzoylacetate* [*β-benzoyloxy-β-phenylacrylate*], m.p. 84—85°, prepared thus and from $CH_2Bz{\cdot}CO_2Et$ by BzCl in C_5H_5N at ~60°, is stable in boiling 50% KOH. $PhSO_2Cl$ does not condense with (I) at room temp.—125°, but causes polymerisation thereof with liberation of EtOH, which then yields $PhSO_2Et$, some $CMe(OEt)_3$, and (V) being also formed. With 1·6N-acid or -phenol in Et_2O, (I)

gives the following yields of (V): HF, PhOH, *p*-$C_6H_4Br{\cdot}OH$ 0, HCl 23, HBr 10, $CCl_3{\cdot}CO_2H$ 37, $CH_2Cl{\cdot}CO_2H$ 42, HCO_2H 35, BzOH 38, AcOH 37, $C_6H_2Br_3{\cdot}OH$ 26, $C_6H_2Cl_3{\cdot}OH$ 21%. R. S. C.

Preparation of monoacylethenones.—See B., 1942, II, 141.

Stereochemistry. I. Steric strains as a factor in the relative stability of co-ordination compounds of boron.—See A., 1942, I, 246.

Manufacture of [lower aliphatic] amines.—See B., 1942, II, 141.

Salts of diethyl*iso*propylamine. S. Caspe (*Amer. J. Pharm.*, 1942, **114**, 56—57).—The prep. of the *picrate*, m.p. 180·6—181·6° (sinters at 179·6°), *hydrochloride*, m.p. 56·5—58°, *methiodide*, m.p. 269—270°, and *platinichloride*, m.p. 210·1—211·1° (sinters at 207°), is described. M.p. are corr. J. N. A.

Diazotisation and nitrosation of amines. V. Effect of lowering the dielectric constant of the reaction mixture. J. C. Earl and N. G. Hills (*J.C.S.*, 1942, 275—277).—The reaction between HNO_2 and aliphatic amines in dioxan–H_2O has been studied. By thus suppressing the dissociation of the amine nitrite it was hoped that the reaction would resemble that of aromatic amines, which is of the second order. With 0·25—0·30 mol. of HCl per mol. of amine or HNO_2 the reaction was bimol. but outside these limits the results are irregular. Diagrams show the effect of variations of HCl and dioxan concns. on the reaction rate (cf. A., 1939, II, 414). W. C. J. R.

Copper and nickel complex ions of diethylenetriamine.—See A., 1942, I, 245.

***N*-Dichlorocarbamates; chlorination reactions.** J. Bougault and P. Charrier (*Compt. rend.*, 1941, **213**, 400—402).—PhOH is transformed by a small excess of $NCl_2{\cdot}CO_2Me$ in AcOH into 2 : 4 : 6 : 1-$C_6H_2Cl_3{\cdot}OH$, and *o*-$OH{\cdot}C_6H_4{\cdot}CO_2Me$ into its 5-Cl-compound. $NCl_2{\cdot}CO_2Me$ (I) and $(Cl{\cdot}[CH_2]_2)_2S$ in C_6H_6 give unstable *αβa'β'-tetrachlorodiethyl sulphide*, b.p. 115°/15 mm., which readily yields HCl and $CHCl{:}CH{\cdot}S{\cdot}CHCl{\cdot}CH_2Cl$. Carbazole and a small excess of (I) in AcOH yield *tetrachlorocarbazole*, m.p. 213°. NH_2Bz and (I) in aq. suspension afford NHClBz, and $CH_2Ph{\cdot}CO{\cdot}NH_2$ gives *phenylacetchloroamide*, m.p. 120°. In alkaline solution 2 : 4-*dichloro*-3 : 5-*diketo*-6-*benzyl*-, m.p. 119°, and -6-*phenylethyl*-, m.p. 130°, -1 : 2 : 4-*triazine* are obtained from the Cl-free parents. 2-*Chloro*-3 : 5-*diketodibenzyl*-1 : 2 : 4-*triazine* has m.p. 153°. (I) and diphenylhydantoin in alkaline solution afford 1 : 3-*dichloro*-5-*diphenylhydantoin*, m.p. 166°. H. W.

Preparation of iminodiacetic and aminotriacetic acid.—See B., 1942, II, 141.

Synthesis of β-alanine. P. Ruggli and A. Businger (*Helv. Chim. Acta.*, 1942, **25**, 35—39).—Hydrogenation of $CN{\cdot}CH_2{\cdot}CO_2Et$ in EtOH saturated with NH_3 in presence of Raney Ni gives a non-homogeneous, undistillable product consisting partly of β-alanineamide. In the absence of NH_3, some of the N of ·CN is eliminated as NH_3. The free acid (I) and its salts (*K*, m.p. 178—179°, and *Na*, m.p. 176—178°, salts) are much more easily hydrogenated than the ester. Hydrogenation of (I) without any addition does not give β-alanine (II) but in presence of NH_4 salt + excess of NH_3 (II) is obtained. The presence of NH_3 is essential for good yields. The best results (75% yield) are obtained by hydrogenating the normal K salt (III) in presence of NH_3–MeOH at 80°/130 atm. In absence of NH_3 considerable amounts of NH_3 and, probably, NH_2Et are obtained from (III). With the NH_4 salt and an excess of NH_3 reduction is facile but Ni passes into solution as a complex. The rate of hydrogenation appears to have a little influence on the yield. H. W.

Kinetics of hydrolysis of carbamide and arginine.—See A., 1942, I, 243.

Pantothenic acid. J. Mittermair (*Angew. Chem.*, 1941, **54**, 51—55).—A literature survey. A. T. P.

Manufacture of β-cyanoacrylic esters.—See B., 1942, II, 142.

New methods of preparative organic chemistry. Thiocyanogenation of organic compounds. H. P. Kaufmann (*Angew. Chem.*, 1941, **54**, 195—199). H. W.

Preparation of nitriles RCN by degradation of acids $CH_2R{\cdot}CO_2H$. G. Darzens and C. Mentzer (*Compt. rend.*, 1941, **213**, 268—281).—Improved yields (75%) of aliphatic nitriles are obtained by pyrolysis (210°) of the Ph oximinoalkyl ketones: $COPh{\cdot}CR{:}N{\cdot}OH$ (I) → RCN + BzOH. This fission is also effected with $SOCl_2$. Aliphatic acids from valeric to lauric acid (I) afford nitriles thus: $CH_2R{\cdot}CO_2H$ → $CH_2R{\cdot}COCl$ → $CH_2R{\cdot}COPh$ → (I). Details are given for the degradation of (I) to undeconitrile. C. S.

Preparation of aliphatic dinitriles.—See B., 1942, II, 182.

Hydroxymethylenemalonitrile and derivatives thereof.—See B., 1942, II, 142.

II.—SUGARS AND GLUCOSIDES.

Transformation of tetramethylglucose-1 : 2-ene into 5-methoxymethylfurfuraldehyde. M. L. Wolfrom, E. G. Wallace, and E. A. Metcalf (*J. Amer. Chem. Soc.*, 1942, **64**, 265—269).—2 : 3 : 4 : 6-Tetramethyl-*d*-glucose-1 : 2-ene (I) (improved prep.) in 3N-HCl at 25° gives 5-methoxymethylfurfuraldehyde (II) (81%), m.p. −8° (lit. −9°), identified as semicarbazone, m.p. 156—157° or (after grinding) 163·5—164·5° (lit. 166—167°, 170°), and oxime, m.p. 97—98° (lit. 103—104°), and by conversion into the acid, m.p. 67·5—68·5° (lit. 67·5—68·5°, 72—73°). (I) is thus not an intermediate in the interconversion of tetramethyl-glucose and -mannose in alkali. Polarimetry discloses formation of a *l*-intermediate; increase in Cu no. follows the initial, and decrease in NaOI consumption follows the second, reaction. At the stage of min. *a*, a little (II) is obtained with much of a substance, $C_6H_8O_4$, which yields a phenylosazone, m.p. 120·5—121·5°, $[\alpha]_D^{21}$ −9° in $CHCl_3$ (O-*acetate*, m.p. 131—132°, hydrolysed by Kunz's method; cf. Bergmann *et al.*, A., 1931, 939), and is probably $CHO{\cdot}CO{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$. R. S. C.

Crystalline modifications of *D*-manno-*D*-galaheptose. Preparation of its derivatives. (Miss) E. M. Montgomery and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 247—254).—95% mannose (prep. from vegetable ivory described), $BaCl_2$ (1·2), and NaCN (1·1 mol.) in H_2O at 5° give Ba *D*-manno-*D*-galaheptonate, $+3H_2O$ (lost in air), $[\alpha]$ (here and below $[\alpha]_D^{20}$) −9·5° in H_2O, which gives the acid, m.p. 149—151°, $[\alpha]$ −74·2° in H_2O, and thence (Na–Hg; 38—44%) *α-D*-manno-*D*-galaheptose (I), which is obtained (cf. Isbell, A., 1937, II, 325; 1938, II, 218) in forms, (*a*) $+H_2O$, m.p. 115—120°, and anhyd., m.p. 145°, $[\alpha]$ +123·8°, and (*b*) anhyd., $[\alpha]$ +124—144° in H_2O (here and below for anhyd. heptose; extrapolated), and gives *compounds*, $+CaCl_2,3H_2O$, m.p. 158°, $[\alpha]$ +122·2°, and $+CaCl_2,4H_2O$ (II), m.p. 141°, $[\alpha]$ +140·8° in H_2O (calc. on heptose). In aq. EtOH at 0° (II) gives β-, $+H_2O$, m.p. 104°, $[\alpha]$ +52·9° in H_2O, and (I) gives *αβ-D-manno-D-galaheptose*, m.p. 132°, $[\alpha]$ +82° in H_2O. In all cases mutarotation to $[\alpha]$ +69° occurs. The β-hexa-acetate (III) with PCl_5 and $AlCl_3$ in boiling $CHCl_3$ gives *α-acetochloro-*, m.p. 119°, $[\alpha]$ +175° in $CHCl_3$ [converted into (III) by AgOAc in warm AcOH], and with HBr–AcOH gives *α-acetobromo-D-manno-D-galaheptose* (84%), m.p. 112°, $[\alpha]$ +208·0° in $CHCl_3$. With Ag_2CO_3–MeOH this gives *β-methyl-D-manno-D-galaheptoside* (90%), m.p. 105°, $[\alpha]$ +8·3° in $CHCl_3$, and thence by $Ba(OMe)_2$ the free *β-heptoside* (91%), m.p. 168°, $[\alpha]$ −5·1° in H_2O (*k* 0·00084 for hydrolysis in 0·05N-HCl at 98°). In boiling 1% HCl–MeOH, (I) gives mixed (5% of β-form isolated) glucosides, which with Ac_2O–C_5H_5N at 0° yield *α-methyl-D-manno-D-galaheptoside*, m.p. 156°, $[\alpha]$ +149·5° in $CHCl_3$, and thence the free *α-heptoside*, m.p. 141°, $[\alpha]$ +178° in H_2O (*k* 0·00078 for hydrolysis as above); milder treatment gives *β-methyl-D-manno-D-galaheptofuranoside* (29·6%), m.p. 115°, $[\alpha]$ −111° in H_2O (*k* 0·022 for hydrolysis as above), the *penta-acetate*, m.p. 78°, $[\alpha]$ −43·5° in $CHCl_3$, of which in H_2SO_4–Ac_2O–AcOH gives *aldehydo-D*-manno-*D*-galaheptose hexa-acetate, m.p. 146°, $[\alpha]$ −34·1° in $CHCl_3$. R. S. C.

Influence of structural changes in the aglucones on the enzymic hydrolysis of alkyl-β-*D*-glucosides. W. W. Pigman and N. K. Richtmyer (*J. Amer. Chem. Soc.*, 1942, **64**, 369—374).—Relative rates of hydrolysis of glucosides in H_2O by sweet almond emulsin are Me 1·00, *n*-amyl 13·1, *n*-hexyl 17·5, *n*-heptyl 31·4, *n*-octyl 29·2, *n*-nonyl (I) 20·0, *cyclo*hexyl (II) 10·8, *cyclo*hexylmethyl 13·6, *β-cyclo*hexylethyl 20·0, Ph 9·2, CH_2Ph 13·2, $Ph{\cdot}[CH_2]_2$ 14·2, and $Ph{\cdot}[CH_2]_3$ 17·2. Hydrolysis in 33 vol.-% MeOH is slower and not unimol. In H_2O it is unimol. for (I) and (II) for the whole reaction. Free $n\text{-}C_7H_{15}{\cdot}OH$ slows, but does not stop, reaction. Correlation of these results with those of Helferich and of Veibel *et al.* (A., 1938, II, 220) is discussed. n-*Amyl*-, m.p. 91·5—93°, $[\alpha]$ −36·3° in H_2O (*tetra-acetate*, m.p. 45·2°, $[\alpha]$ −22·1° in $CHCl_3$), *n*-hexyl-, m.p. 90—92°, $[\alpha]$ −34·5° in H_2O (*tetra-acetate*, m.p. 50·5—51·5°, $[\alpha]$ −20·2° in $CHCl_3$), n-*heptyl*-, m.p. 74—77° (anisotropic), $[\alpha]$ −34·2° in H_2O (*tetra-acetate*, m.p. 66—68·5°, $[\alpha]$ −20·5° in $CHCl_3$), *n*-octyl-, m.p. 62—65° (anisotropic), $[\alpha]$ −34·0° in H_2O (tetra-acetate, m.p. 62·8—63·0°, $[\alpha]$ −20·5° in $CHCl_3$), *n*-nonyl-, m.p. 67·5—70° (anisotropic), $[\alpha]$ −34·4° in H_2O (tetra-acetate, m.p. 40·7—41·5°, $[\alpha]$ −19·5° in $CHCl_3$), *n*-decyl-, m.p. 73—74° (anisotropic), $[\alpha]$ −28·3° in MeOH, sparingly sol. in H_2O (tetra-acetate, m.p. 49·5—51°, $[\alpha]$ −19·5° in $CHCl_3$), and β-cyclo*hexylethyl*-, m.p. 99—101°, $[\alpha]$ −32·3° in H_2O (*tetra-acetate*, m.p. 75—75·5°, $[\alpha]$ −21·1° in $CHCl_3$). -d-*glucoside* are described. M.p. are determined on a microscope stage. $[\alpha]$ are $[\alpha]_D^{20}$. R. S. C.

Heart glucosides. XVIII. Scilliroside, a poison of the red squill, specifically active towards rodents. A. Stoll and J. Renz (*Helv. Chim. Acta*, 1942, **25**, 43—64).—The material is dried at ~60°, the abs. EtOH extract evaporated, and the residue dissolved in H_2O and treated with freshly pptd. $Pb(OH)_2$; the filtrate is conc. and extracted first with $CHCl_3$ to remove lipins and then with $CHCl_3$ + 20% of $Bu^{\alpha}OH$, which removes the glucosides. The residue from the extract is suspended in H_2O and shaken with $CHCl_3$ followed by $CHCl_3$ + 5% of $Bu^{\alpha}OH$. *Scilliroside* (I) is then found in the org. mixture and the true heart glucosides remain in the H_2O. (I), $C_{32}H_{44}O_{12},0{\cdot}5H_2O$, has m.p. (indef.) 168—170°, decomp. ~200°, $[\alpha]_D^{20}$ −59·7° in MeOH. It gives a negative Legal test and a not very characteristic, pale brown ring in the Keller–Kiliani reaction. The

Liebermann sterol reaction is violet → green → blue-green. The Baljet and Rosenheim reactions are negative. It does not give a colour with $FeCl_3$. Boiling Fehling's solution is slowly reduced. Quant. alkaline hydrolysis of (I) under mild conditions consumes 2 mols. of KOH, one of which is required for the opening of the unsaturated lactone ring and the other for removal of Ac, confirmed by isolation of AcOH as AgOAc. (I) is transformed by Ac_2O and C_5H_5N at room temp. into the *tetra-acetate* (II), m.p. 199°, $[\alpha]_D^{20}$ −48·6° in MeOH, which contains 2 OH (Zerevitinov). Alkali very readily opens the lactone ring of (II) and splits off the Ac of (I), but NH_3–MeOH at 0° transforms (II) into (I). *Scilliroside tetrapropionate*, m.p. 188°, $[\alpha]_D^{20}$ −47·4° in MeOH, and *tetrabenzoate*, m.p. 168—170°, are described. Hydrolysis of (I) by mineral acid is relatively difficult and leads to glucose, and an aglucone which has not been obtained cryst. or converted into homogeneous derivatives. Hydrogenation (Pd in EtOH) of (I) results in removal of Ac and saturation of two double linkings, thus leading to the *compound*, $C_{30}H_{46}O_{10}$, m.p. 284°, $[\alpha]_D^{20}$ +34° in MeOH; apparently, a third double linking is also present. (I) is very closely related to the heart glucosides, particularly scillaren *A* (III), and its ultra-violet spectrum proves that its skeleton and the doubly unsaturated lactone ring are similar to those of (III). The abs. lethal dose of (I) is 1·2 mg. per kg. for male and 0·6 mg. for female rats. (I) shows typical cardioactive properties towards the isolated frog's heart and agrees in all respects with a scillaren standard prep. (I) occurs exclusively in the red squill and here predominates greatly over the other glucosides. The white squill contains mainly scillaren *A* and *F* in addition to a series of glucosides which appear to be absent from the red variety. M.p. are corr., vac. H. W.

Steroids. XXXIII. Glucosides of deoxycorticosterone. K. Miescher, W. H. Fischer, and C. Meystre (*Helv. Chim. Acta*, 1942, **25**, 40—42).—Deoxycorticosterone (I) is converted by acetobromoglucose and dry Ag_2CO_3 in C_6H_6–Et_2O into the *tetra-acetyl-β-glucoside* (II), m.p. 175—176°, $[\alpha]_D^{20}$ +80°±0·8° in $COMe_2$. If Ag_2O is used in place of Ag_2CO_3 3-ketoætiocholenic acid is also formed. (II) is hydrolysed by K_2CO_3 in MeOH to *deoxycorticosteroneglucoside*, m.p. 190—195°, $[\alpha]_D^{20}$ +109°±2° in MeOH, which is sol. in H_2O and retains the full physiological activity of (I). M.p. are corr. H. W.

Constitution of arabogalactan. II. Isolation of hepta- and octa-methyl-6-galactosidogalactose by partial hydrolysis of methylated arabogalactan. E. V. White (*J. Amer. Chem. Soc.*, 1942, **64**, 302—306; cf. A., 1942, II, 134).—Arabogalactan (improved prep.) consists of a highly branched galactose chain united by 1 : 3- and 1 : 6-O-linkings with terminal arabofuranose and galactopyranose units attached to position 6 of galactose anhydride units. It is not possible to remove only the arabinose by partial hydrolysis. Dry HCl–MeOH gives, by partial hydrolysis, mixtures separable into fractions (*A*) sol. and (*B*) insol. in light petroleum. Decrease in the OMe content of *B* as hydrolysis progresses is illustrated. *A* contains 2 : 3 : 5-trimethyl-*l*-arabinoside, 2 : 3 : 4 : 6-tetramethyl-*d*-galactosidc, 2 : 3 : 4-trimethyl-*d*-galactoside, *octa-* (I), m.p. 101°, $[\alpha]_D^{25}$ +42·9° in MeOH [hydrolysed to 2 : 3 : 4 : 6-tetra- (II) and 2 : 3 : 4-tri-methyl-*d*-galactose (III)], and *hepta-methyl*-6-d-(?β-)*galactosidogalactose*, m.p. 141° [hydrolysed to (II) and 2 : 4-dimethyl *d*-galactose (IV) and giving (I) by methylation]. *B* contains (IV) and a little (III), but after methylation, followed by hydrolysis, gives (III) and the 2 : 4 : 6-Me_3 derivatives. R. S. C.

Constitution of agar. W. G. M. Jones and S. Peat (*J.C.S.*, 1942, 225—231).—It is suggested that the agar polysaccharide (I) consists of a linear association of nine *d*-galactopyranose residues mutually combined by 1 : 3-glycoside linkings and an *l*-galactopyranose sulphuric ester 1 : 4-linking. This chain must be present as a repeating unit since tetramethyl-*d*-galactose (II) is not an invariable constituent of methylated (I). During the commercial prep. of (I) hydrolysis of the sulphuric ester occurs, a 3 : 6-anhydro-ring being formed; this structure is probably present in the S-free acetylated or methylated (I). This view is supported by the presence of 2 : 4 : 6-trimethyl-*d*-galactoside and 2-methyl-3 : 6-anhydro-1-methylgalactoside (III) in the methanolysis product of methylated (I). (III) has not been isolated but a fraction has been obtained which on further methylation gives 2 : 4-dimethyl-3 : 6-anhydro-*l*-galactoside (IV), the increase in OMe agreeing with (III) → (IV). Methylated (I) has been resolved into two components, one of higher ash content being acidic. It is probably formed by the fission in acid media of a glycoside linking to give CHO which passes into CO_2H in air. The structure of the acid is confirmed by the presence in the hydrolysate of the fully methylated acid of (II) and 2 : 5-*dimethyl*-3 : 6-*l*-*galactonic acid*. This also proves that the *l*-galactose residue must be linked to the chain at $C_{(1)}$. The biological synthesis of (I) is discussed. W. C. J. R.

Multiple amylose concept of starch. II. Amylopectin and amylose. R. W. Kerr, O. R. Truebell, and G. M. Severson (*Cereal Chem.*, 1942, **19**, 64—81; cf. B., 1941, **III**, 328).—The proportion of starch not saccharified after diastatic conversion was determined by a refined procedure for corn, tapioca, and potato starches. This unsaccharified portion (amylopectin), not const. in quantity from the three starches, was not identical with γ-amylose. In an attempt to prepare pure amylose (*i.e.*, a material converted quantitatively into maltose by β-amylase), starch was fractionated by previously known methods (electrophoresis, extraction by hot H_2O, freezing and thawing) and by new methods [pptn. by EtOH and pptn. of starch acetate (I)], but in no case did the products completely answer the requirements. The product showing the highest degree of diastatic conversion was obtained by fractional pptn. of (I). The amylopectin–amylose concept of Maquenne is still considered to be hypothetical. N. L. K.

III.—HOMOCYCLIC.

Density distribution and zero-point energy of the *B*-electrons of aromatic compounds.—See A., 1942, I, 197.

Catalytic isomerisation of monocyclic hydrocarbons in presence of molybdenum disulphide. P. V. Putschkov (*J. Phys. Chem. Russ.*, 1940, **14**, 1319—1320).—MoS_2 at 400° in H_2 at 190—300 atm. transforms *cyclo*hexane (I) into methyl*cyclo*pentane (II), *n*-hexane, and *iso*hexanes; methyl*cyclo*hexane into 1 : 2- (III) and 1 : 3-dimethyl-*cyclo*pentane (IV); hexahydromesitylene into *n*-C_5H_{12} and other low-boiling paraffins; C_6H_6 into much (II) and less (I); PhMe into (III) and (IV); and PhEt into homologues of *cyclo*pentane. J. J. B.

Oxidation of pyrolytic distyrene. L. Marion (*Canad. J. Res.*, 1941, **19, B**, 205—211).—Distillation (vac.) of polystyrene (1150), mol. wt. 8000, gives styrene (I) (403), distyrene (II) (161·5), "tristyrene" (III) (390·7), and 1 : 3 : 5-$C_6H_3Ph_3$ (7·5 g.) [obtained with (I) and (II) when (III) is distilled at atm. pressure]. With $KMnO_4$ in $COMe_2$, (II) gives Ph·$[CH_2]_2$·COPh (IV), BzOH, and *α-hydroxy-αγ-diphenyl-*n*-butyric acid* (V), m.p. 147° (isolated as Et ester, b.p. 184—187°/4 mm.; *Me* ester). (V) is further oxidised by $KMnO_4$–$COMe_2$ to (IV) and with HBr–AcOH, followed by Na–Hg, gives *αγ*-diphenyl-γ-butyrolactone. It is concluded that (II) contains Ph·$[CH_2]_2$·CPh:CH_2 (first oxidised to the glycol) and its isomerides, notably CHPh:CH·CHPhMe whence is derived the BzOH formed on oxidation. $CH_2Br·CO_2Et$, (IV), and Zn in C_6H_6–Et_2O give *Et β-hydroxy-ββδ-diphenyl-*n*-valerate*, m.p. 79·5°, hydrolysed (KOH) to the *acid*, m.p. 155°. R. S. C.

Catalytic oxidation of naphthalene and its derivatives in the gas phase. A. Pongratz, F. Bassi, E. Fuchs, S. Süss, H. Wüstner, and K. Schöber (*Angew. Chem.*, 1941, **54**, 22—26).—The mechanism of the oxidation of $C_{10}H_8$ and its derivatives by atm. O_2 in presence of V_2O_5 (prep. described) has been investigated. 2-$C_{10}H_7Cl$ gives 47% of 4 : 1 : 2-$C_6H_3Cl(CO)_2O$, 53% of *o*-$C_6H_4(CO)_2O$ (I); 1-$C_{10}H_7Cl$ gives 97% of (I) and 3% of 3 : 1 : 2-$C_6H_2Cl(CO)_2O$. 1-$C_{10}H_7·NO_2$ gives 80% of *o*-$C_6H_4(CO)_2NH$ (II); 2-$C_{10}H_7·NO_2$ gives 52% of 4 : 1 : 2-$NO_2·C_6H_3(CO)_2O$, 46% of (I), but no (II). α- and β-$C_{10}H_7·NH_2$ and α-$C_{10}H_7·CN$ give (II). β-$C_{10}H_7·CN$ gives a N-containing carboxylic acid. Both α- and β-N derivatives split off part of their N as HCN. This is probably formed by the reaction CO (radical) + NH_3 = HCN + H_2O. In an indifferent gas (N_2) the quantity of CO_2 in the N_2 phase is always > would be expected if the oxidation proceeded only to (I). The primary oxidation product is probably 1 : 2 : 3 : 4-$C_{10}H_4(OH)_4$ (III), and the reaction is $C_{10}H_8 + 4O \rightarrow$ (III) → (O_2) 2 : 3 : 1 : 4-$C_{10}H_4(OH)_2O_2 \rightarrow$ (19O)$10CO_2 + 3H_2O$ or (4O) (I) + $2CO_2 + H_2O$. The temp. at which the catalyst becomes active varies with its treatment. A. J. M.

Effect of structure on reactivity : nuclear substitution of benzene derivatives. H. F. McDuffie, jun., and G. Dougherty (*J. Amer. Chem. Soc.*, 1942, **64**, 297—299).—The effects of structure on the rates of nuclear substitution have been investigated using the Friedel–Crafts reaction of AcCl with C_6H_6 derivatives in presence of anhyd. $AlCl_3$. The relative reactivities of pairs of C_6H_6 derivatives have been determined for the following pairs: PhMe–C_6H_6; *o*-C_6H_4MeCl–PhCl; *o*-C_6H_4MeCl–C_6H_6; PhCl–*p*-C_6H_4MeCl; PhCl–PhBr; *m*-xylene–PhMe; mesitylene–PhMe. For monosubstituted derivatives the ascertained reactivities agree well with available data for nitration, substituent consts., and rates calc. from dipole moments of monosubstituted benzenes and confirm the ionic mechanism of the reaction. W. R. A.

Diradicals. E. Müller (*Angew. Chem.*, 1941, **54**, 192—193).—The following compounds have been prepared with the object of ascertaining whether the calculation of magnetism is applicable to compounds such as the Tschitschibabin hydrocarbon (I). The *compound* (I), (2 : 6 : 4-$C_6H_2Cl_2·CR_2)_2$ (R = *p*-C_6H_4Ph), is colourless and diamagnetic when solid but gives dark brown, strongly paramagnetic solutions in C_6H_6 corresponding with 75% fission (c = 1·9). (I) is a true diradical with *para* "free valencies" which represents a double diphenylxenylmethyl in all its behaviour. Correspondingly the atropisomeric Ph_2 derivatives with xenyl Ph or Ph_2 residues at the "radical" C atoms are also true diradicals. It follows therefore that when there is complete independence of the two single electrons, the theoretical val. of 2 magnetons required for a true diradical is attained. The *substance* $C_6H_4(C_6H_4·CR_2)_2$ is a green solid giving intense, dark green C_6H_6 solutions very sensitive to air. The val. of paramagnetism in 1·8% solution in C_6H_6 at 20° or 80° is ~1 magneton.

Correspondingly the compounds in which R = xenyl and Ph or R = Ph and Ph as well as the *compound*, $([C_6H_4]_2{\cdot}CR_2)_2$, give vals. <1 magneton. Substances of this type are intensely coloured, very reactive, and not analogous to the triarylmethyls. The term "diradicaloid" is preferred for such compounds. To these compounds belong 3 : 8- and 3 : 10-diphenylpyrenylmethyl and, possibly, di-*pp'*-diphenylmethylditolyl. According to Schwab *et al.* (A., 1938, I, 625) the *para*-H_2 transformation by free radicals of the CPh_3 class can be used as a method of determination on the basis of a sp. transformation const. $a = 2{\cdot}6 \times 10^{-2}$ hr.$^{-1}$ (m-mol. per l.)$^{-1}$. For diradicals *a* is doubled. Schwab's vals. for (I) and $(CH{\cdot}C_6H_4{\cdot}CPh_2)_2$ are $\gg$ those determined by the magnetic method and this is true also for the diradicals and diradicaloids described above. If *a* is multiplied by four in the case of diradicals, the results of the two methods harmonise. Hence Schwab's method is not a certain criterion of diradical content. The author's definition that a substance is a radical or diradical if it exhibits paramagnetism is applicable to all radicals. H. W.

β-Phenyl-αβ-dialkylethylamines. Alkylation of phenylacetone. C. M. Suter and A. W. Weston (*J. Amer. Chem. Soc.*, 1942, **64**, 533—536).—Methylation of $CH_2Ph{\cdot}COMe$ (I) by MeI in NaOEt–EtOH gives a mixture [mainly unchanged (I)] but in NaOPrβ–PrβOH gives 74% of $CHPhMe{\cdot}COMe$ (II), b.p. 106—107°/22 mm. $CHPhEt{\cdot}COMe$ (55%), b.p. 110°/18 mm., and $CHPhPr^n{\cdot}COMe$ (55%), b.p. 114—115°/13 mm. (semicarbazone, new m.p. 137—137·5°), are similarly obtained in PrβOH, but $CPhMe_2{\cdot}COMe$, b.p. 99—99·5°/12 mm., is obtained from (II) only in KOBu$^\gamma$–Bu$^\gamma$OH–PhMe (50% yield). Relative acidities are thus EtOH > (I) > PrβOH > (II) > Bu$^\gamma$OH. When boiled with $HCO{\cdot}NH_2$ or $HCO{\cdot}NHMe$ (slower reaction), the ketones give $CHPhR{\cdot}CHMe{\cdot}NR'{\cdot}CHO$ (R and R' = H or Me), hydrolysed by acid or alkali to $CHPhR{\cdot}CHMe{\cdot}NHR'$; the yield by alkaline hydrolysis decreases as the mol. wt. of R increases. Thus are obtained *β-amino-γ-phenyl-n-butane* (III) (60%), b.p. 118—119°/19 mm. (*hydrochloride*, m.p. 136—139°, and an impure isomeride), *-n-pentane* (63%), b.p. 118°/19 mm. (*hydrochloride, diastereoisomerides*, m.p. 171—172° and 258—261°), *-n-hexane* (68·5%), b.p. 116°/15 mm. (*hydrochloride, diastereoisomerides*, m.p. 120—123°, and 250—253°; *CHO* derivative, b.p. 162·5—164°/6 mm.), and *-γ-methylbutane* (IV) (76·5%), b.p. 105—106°/13 mm. (*hydrochloride*, m.p. 213·5—215°), *β-methylamino-γ-phenyl-n-butane* (16%), b.p. 111°/24 mm. (*hydrochloride*, m.p. 116—120°), and $CH_2Ph{\cdot}CHMe{\cdot}NHMe$ (22%). *n* and *d* of the ketones and amines are given. Introduction of β-Me into $Ph{\cdot}[CH_2]_2{\cdot}NH_2$ reduces the toxicity without affecting the pressor activity; introduction of a second β-Me [as in (IV)] slightly increases the toxicity compared with (III). In rabbits all the amines have approx. equal pressor activity (greater for diastolic than for systolic pressure), but in dogs $CH_2Ph{\cdot}CHMe{\cdot}NH_2$ and (III) are most effective. Some of the amines have analeptic activity. R. S. C.

Colour reactions of organic nitrogen compounds with selenious acid–sulphuric acid solutions. B. T. Dewey and A. H. Gelman (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 361—362).—The colour reactions of 45 amines and related compounds with H_2SO_4–H_2SeO_3 are described. J. D. R.

Quaternary ammonium salts and their decomposition products. A. Zaki and H. Fahim (*J.C.S.*, 1942, 270—273; cf. A., 1930, 905).—The following are prepared from the *tert.* amine and Me_2SO_4 at 100° (bath) (sometimes in boiling C_6H_6), with subsequent conversion into the picrate, then (conc. HCl) the chloride, and thence (conc. aq. KI, $NaClO_4$, or Br–AcOH) the iodide, perchlorate, or perbromide, respectively: o-, m.p. 167—168°, m-, m.p. 150—151° [*chloride* (I), m.p. 230—235° (decomp.); perbromide, m.p. 120° (decomp.)], and *p-nitrophenyltrimethylammonium picrate*, m.p. 182—183° [*chloride* (II), m.p. 183—184° (decomp.); *iodide*, m.p. 161° (decomp.); *perchlorate*, m.p. 181—182°; perbromide, m.p. 154—157° (decomp.)]; *o-tolyl-*, m.p. 198—199° [chloride (III), m.p. ~84—85° (cf. Groenewoud *et al.*, A., 1935, 76); iodide, volatilises at 225°], and *o-anisyltrimethylammonium perchlorate*, m.p. 224—225° [impure chloride (IV), *loc. cit.*]: *4-nitro-2-methoxy-*, m.p. 174—175° [*chloride* (V), m.p. ~183° (decomp.); *iodide*, m.p. 156—157° (decomp.); *perchlorate*, m.p. 207—208°; perbromide, m.p. 135° (decomp.)], and *4-nitro-2-methyl-phenyltrimethylammonium picrate*, m.p. 197—198° (decomp.) [*chloride* (VI), m.p. 174—175° (decomp.); *iodide*, m.p. ~145° (decomp.); *perchlorate*, m.p. 186—187°; perbromide, m.p. 121—122° (decomp.)]. o-$NO_2{\cdot}C_6H_4{\cdot}NMe_3Cl$ (from picrate and conc. HCl) immediately decomposes to o-$NO_2{\cdot}C_6H_4{\cdot}NMe_2{,}HCl$. Thermal decomp. at > the m.p. of the above chlorides affords the respective *tert.* base and MeCl; with NaOEt, (I), (III), or (IV) gives the base + MeOEt, but (II), (V), and (VI) afford NMe_3 and the corresponding phenetole derivatives. A. T. P.

Antibacterial substances allied to sulphanilamide. T. Dewing, W. H. Gray, B. C. Platt, and D. Stephenson (*J.C.S.*, 1942, 239—244).—Non-basic substituents introduced into the mol. of p-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ (I) give substances of lower or equal activity. (I) yields (Schotten–Baumann) N^4-*benzoyl-*, m.p. 284°, and N^1N^4-*dibenzoyl-sulphanilamide*, m.p. 268—270° (more conveniently prepared in C_5H_5N). *Sulphanilyl-myristamide*, m.p. 126°, and *-adipamic acid*, m.p. 178°, are obtained from p-$NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ and the respective chloride in C_5H_5N, followed by hydrolysis with aq. NaOH. Chaulmoogric acid affords *sulphanilylchaulmoogramide*, m.p. 80—90° [hydrogenated (C–Pd; $COMe_2$) to a H_2-derivative, m.p. 78—80°], and *disulphanilylethyleneguanidine*, formula probably

p-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}N{\cdot}[CH_2]_2{\cdot}N(SO_2{\cdot}C_6H_4{\cdot}NH_2$-$p){\cdot}C{:}NH$, m.p. 178—180°, is obtained from ethyleneguanidine hydrobromide and p-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ (II) in aq. Na_2CO_3, followed by hydrolysis of the Ac derivative, m.p. 245°. Glutamic acid and (II) in aq. NaOH, followed by hydrolysis of the Ac compound, m.p. 142° (decomp.), afford *sulphanilylglutamic acid*, m.p. 192—194° (*Na*$_2$ salt), and $Br{\cdot}[CH_2]_2{\cdot}NH_2{,}HBr$ similarly (in aq. Na_2CO_3) gives an Ac compound, m.p. 161—164°, hydrolysed (6N-HCl) to p-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}[CH_2]_2{\cdot}Br$, m.p. 69—70°, converted by C_5H_5N–EtOH into *sulphanilamidoethylpyridinium bromide*, m.p. 218°. Sulphanilylglycine and PhCHO–EtOH give *p-benzylideneaminobenzenesulphonylglycine*, m.p. 185—186°. 3 : 2 : 1-$OH{\cdot}C_6H_3(Hg{\cdot}OAc){\cdot}CHO$ and (I) in boiling AcOH–EtOH yield *2'-acetoxymercuri-3'-hydroxybenzylidenesulphanilamide*, m.p. 282°. 8-Hydroxyquinoline and p-$C_6H_4Cl{\cdot}NO_2$–KOH at 180° give *p-nitrophenyl 8-quinolyl ether*, m.p. 170°. p-$NO_2{\cdot}C_6H_4{\cdot}OPh$ and $ClSO_3H$ at 10° or 95°, followed by aq. NH_3, yield *4-p-nitrophenoxybenzenesulphonamide*, m.p. 129°, or *p-nitrophenoxybenzenedisulphonamide*, m.p. 270°, respectively. (p-$NH_2{\cdot}C_6H_4)_2SO_2$ (III) and p-$NO_2{\cdot}C_6H_4{\cdot}COCl$ in C_5H_5N yield *4 : 4'-bis-(p-nitrobenzamido)diphenylsulphone*, m.p. 346°. *d*-Glutamic acid (IV) and m-$C_6H_4Me{\cdot}NH_2$ or p-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ at 160—170° yield *2-pyrrolidone-5-carboxy-m-toluidide* (V), m.p. 147°, or *-p-nitroanilide*, m.p. 225°, respectively, and (V) with $ClSO_3H$ at 50—60° followed by conc. aq. NH_3 affords a (?-)*sulphonamide*, m.p. 222°. (IV) and α-$C_{10}H_7{\cdot}NH_2$ at 185—190°, yield *2-pyrrolidone-5-carboxy-α-naphthalide*, m.p. 207°, or at 210° an *isomeride*, m.p. 224°. *l*-2-Pyrollidone-5-carboxyanilidc and $ClSO_3H$ at 60—70° give a substance, m.p. 173° (decomp.), converted by 2-aminopyridine in dioxan at 95° into *2-(2'-pyrrolidone-5'-carboxy-4''-aminobenzenesulphonamido)pyridine*, m.p. 273°. (III) diazotised in 17% HCl at −7°, and coupled, yields *diphenylsulphone-4 : 4'-bisazo-β-naphthol* (VI), m.p. 304°, and *-salicylic acid* (VII), m.p. 316° (decomp.), respectively; (VI) is inactive, whereas (VII) retains the action of (I) against streptococcus and is as active as sulphapyridine against pneumococcus. *2 : 2'-Dipyridylsulphone*, m.p. 216°, is prepared from *2 : 2'-dipyridyl sulphide dihydrobromide* (cf. Kolmer *et al.*, A., 1938, III, 140), m.p. 274°, and $K_2Cr_2O_7$–aq. AcOH–H_2SO_4. Quininic acid and $SOCl_2$ at 100°, followed by (I)–C_5H_5N at 110°, give N^4-*quininoylsulphanilamide*, m.p. 255°, also obtained from quininanilide and $ClSO_3H$, followed by NH_3. Antipyrine and $ClSO_3H$ at −15°, then at 90°, followed by conc. aq. NH_3, yield *1-phenyl-2 : 3-dimethyl-5-pyrazolone-x-sulphonamide*, m.p. 239° (corresponding SO_3Na derivative). Dihydrochaulmoogric acid and $SOCl_2$ at 90°, followed by (I)–C_5H_5N, afford N^4-*dihydrochaulmoogrylsulphanilamide*, m.p. 208°. 2-Aminopyridine and CH_2O–$NaHSO_3$ at 80° yield *Na 2-aminopyridine-N-methylenebisulphite*, +1·5H_2O, m.p. 282° (decomp.). p-$NO_2{\cdot}C_6H_4{\cdot}SOCl$ and MeOH–C_5H_5N or $N_2H_4{,}H_2O$–EtOH yield *Me*, m.p. 47°, or *Et* p-*nitrobenzenesulphinate*, m.p. 49—51°, respectively. p-$NO_2{\cdot}C_6H_4{\cdot}SCl$–$NH_3$–$Et_2O$ give p-*nitrobenzenesulphenamide*, m.p. 101—103°, together with some $(p$-$NO_2{\cdot}C_6H_4{\cdot}S)_2$. p-$NO_2{\cdot}C_6H_4{\cdot}SO_2Cl$ and p-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ or p-$NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_4{\cdot}NH_2$-$p$ in C_5H_5N give *p-nitrobenzenesulphon-p'-nitroanilide*, m.p. 171—173°, or *4-nitro-4'-(p-nitrobenzenesulphonamido)diphenyl sulphide*, m.p. 190°, respectively. A. T. P.

Di(aminoarylsulphon)amides.—See B., 1942, III, 157.

***NN'*-Diarylarylenediamines.**—See B., 1942, II, 217.

Tensimetric determination of higher ammoniates of complex salts.—See A., 1942, I, 209.

Preparation of benzenediazonium salts. W. Smith and C. E. Waring (*J. Amer. Chem. Soc.*, 1942, **64**, 469—470).—PhN_2Cl and $PhN_2{\cdot}HSO_4$ are obtained rapidly and nearly quantitatively by bubbling OEt·NO into $NH_2Ph{,}HCl$– or $NH_2Ph{,}H_2SO_4$–AcOH–dioxan at <0° and then adding more dioxan at room temp. PhN_2Cl is stable under dioxan at room temp. R. S. C.

Decomposition reactions of the aromatic diazo-compounds. X. Mechanism of the Sandmeyer reaction. W. A. Waters (*J.C.S.*, 1942, 266—270; cf. A., 1940, II, 14).—Decomp. reactions of the aromatic diazo-compounds are of three types, viz., (*a*) decomp. of diazonium cations, giving aryl cations, (*b*) decomp. of co-valent diazo-compounds, giving two neutral radicals, and (*c*) catalysed decomp. of diazonium cations, involving a single electron transference, yielding neutral aryl radicals ($ArN_2^+ + e \rightarrow Ar^{\cdot} + N_2$). Sandmeyer and Gattermann reactions are represented as type (*c*), involving cyclical electron transferences facilitated by the easy release of an electron from a cuprous cation or from metallic Cu. An examination of relative oxidation–reduction potentials affords an explanation of the almost unique character of Cu^I salts and of Cu, and a discussion of the side reactions (*e.g.*, formation of *s*-diaryls) which occur in diazo decomps. of this group further supports the view that tran-

sient neutral aryl radicals are involved. Theoretical aspects are discussed. A. T. P.

Reactions of *n*-butyl bromide with sodium salts of phenol, thiophenol, and *n*-butyl mercaptan.—See A., 1942, I, 243.

Alkylphenols.—See B., 1942, II, 217, 218.

Molecular structure in relation to œstrogenic activity : polynuclear analogues of γδ-di-*p*-hydroxyphenyl-*n*-hexane (" hexœstrol "). N. R. Campbell and F. W. Chattaway (*Proc. Roy. Soc.*, 1942, **B**, **130**, 435—447; see also A., 1942, III, 523).—(CHEtAr)$_2$ (Ar = *p*-C_6H_4Ph; *p*-OPh·C_6H_4; *p-p'*-OH·C_6H_4·C_6H_4·; *p-p'*-OH·C_6H_4·O·C_6H_4·; α- and β-$C_{10}H_7$; 4 : 1- and 6 : 2-OH·$C_{10}H_6$·) are prepared (yields variable) by a Wurtz reaction on CHEtArBr (not isolated; formed direct from CHEtAr·OH), but could not be obtained by hydrogenation of (CArCHMe)$_2$ (cf. A., 1940, II, 79). Phenolic OH are protected as OMe with subsequent demethylation by EtOH–KOH at 210°. *p*-C_6H_4Ph·COEt (**I**) [from Ph_2, $(EtCO)_2O$, and $AlCl_3$ in $PhNO_2$ at 0°—room temp.] is reduced (Al–Hg, moist Et_2O) to γδ-*di*-p-*diphenylyl*-n-*hexane*-γδ-*diol*, m.p. 240°, dehydrated ($KHSO_4$) to γδ-*di*-p-*diphenylyl*-Δ$^{\beta\delta}$-*hexadiene*, m.p. 151°. Reduction [Al(OPr$^\beta$)$_3$, Pr$^\beta$OH] of (**I**) gives impure *p*-C_6H_4Ph·CHEt·OH, the bromide [prep. by HBr–PhMe at <−5° and then drying ($CaCl_2$); general method] of which with Na in PhMe at 55—60°/8 hr. and then at room temp./40 hr. affords γδ-*di*-p-*diphenylylhexane*, m.p. 254°. p-*Phenoxypropiophenone*, m.p. 38°, similarly yields γδ-*di*-p-*phenoxyphenyl*-n-*hexane*-γδ-*diol*, m.p. 175°, dehydrated (boiling Ac_2O–AcCl) to the -Δ$^{\beta\delta}$-*hexadiene*, m.p. 132—133°, which is reduced (H_2, Pt–C, AcOH) to a γδ-*di*-p-*phenoxyphenylhexene*, m.p. 118°. α-p-*Phenoxyphenyl*-n-*propyl alcohol*, b.p. 150°/0·2 mm., affords (as above) γδ-*di*-p-*phenoxyphenylhexane*, m.p. 142°. p-*Anisylpropiophenone*, m.p. 143° [from *p*-C_6H_4Ph·OMe, $(EtCO)_2O$, and $AlCl_3$ in $C_2H_2Cl_4$], gives γδ-*di*-(4'-*methoxy*-4-*diphenylyl*-n-*hexane*-γδ-*diol*, forms, m.p. 178° and 264°, both dehydrated ($KHSO_4$) to γδ-*di*-(4'-*methoxy*-4-*diphenylyl*)-Δ$^{\beta\delta}$-*hexadiene*, m.p. 152°. The Wurtz reaction with the bromide of α-4'-*methoxy*-4-*diphenylyl*)-n-*propyl alcohol*, m.p. 93°, gives some 4-*methoxy*-4'-*propenyldiphenyl*, m.p. 150°, in addition to the *Me*$_2$ *ether*, m.p. 260°, of γδ-*di*-(4'-*hydroxy*-4-*diphenylyl*)*hexane*, m.p. 240°. 4'-*Methoxy*-4-*phenoxypropiophenone*, m.p. 64° [from *p*-OMe·C_6H_4·OPh, $(EtCO)_2O$, and $AlCl_3$ in $C_2H_2Cl_4$], yields γδ-*di*-(4'-*methoxy*-4-*phenoxyphenyl*)-n-*hexane*-γδ-*diol*, m.p. 200°, and impure α-4'-methoxy-4-phenoxyphenyl-*n*-propyl alcohol, b.p. 182—188°/1 mm.; the latter leads to the *Me*$_2$ *ether*, m.p. 146°, of γδ-*di*-(4'-*hydroxy*-4-*phenoxy*)-*hexane*, m.p. 198°. 6 : 2-OMe·$C_{10}H_6$·COEt (prep. from 2-$C_{10}H_7$·OMe, EtCOCl, and $AlCl_3$ in $PhNO_2$ at 0°—room temp.; with $AlBr_3$ in C_6H_6 gives 6-*hydroxy*-2-*naphthyl Et ketone*, m.p. 158°) affords γδ-*di*-6-*methoxy*-2-*naphthyl*-n-*hexane*-γδ-*diol*, m.p. 248°, and α-6-*methoxy*-2-*naphthyl*-n-*propyl alcohol*, m.p. 50°. The Wurtz reaction with 6 : 2-OMe·$C_{10}H_6$·CHEtBr at 60—70° results in loss of HBr (whence 6-*methoxy*-2-*propenylnaphthalene*, m.p. 96°) but at 50—60° the *Me*$_2$ *ether*, m.p. 255°, of γδ-*di*-6-*hydroxy*-2-*naphthylhexane*, m.p. 253°, results. 4 : 1-OMe·$C_{10}H_6$·COEt [from 1-$C_{10}H_7$·OMe, $(EtCO)_2O$, and $AlCl_3$ in CS_2] affords α-4-*methoxy*-1-*naphthyl*-n-*propyl alcohol*, m.p. 68—70°, b.p. 150°/0·2 mm., and thence the *Me*$_2$ *ether*, m.p. 209°, of γδ-*di*-4-*hydroxy*-1-*naphthylhexane*, m.p. 224°. γδ-*Di*-1-*naphthylhexane*, m.p. 155°, is prepared from crude 1-$C_{10}H_7$·CHEt·OH. 2-$C_{10}H_7$·COEt [from $C_{10}H_8$, $(EtCO)_2O$, and $AlCl_3$ in $PhNO_2$ at 0°—room temp.] leads to α-2-*naphthyl*-n-*propyl alcohol*, m.p. 37°, and γδ-*di*-2-*naphthylhexane*, m.p. 198°. Acenaphthenequinone and *p*-OMe·C_6H_4·MgBr give 7 : 8-*dihydroxy*-7 : 8-*dianisylacenaphthene*, m.p. 162°, rearranged (boiling HCO_2H or AcOH–aq. HCl) to 7 : 7-*dianisyl*-8-*acenaphthenone*, m.p. 151°, which is demethylated ($AlCl_3$ in C_6H_6) to 7 : 7-*di*-p-*hydroxyphenyl*-8-*acenaphthenone*, m.p. 240—241°. It is probable that all the analogues of hexœstrol (**II**) [the less fusible form of (*p*-OH·C_6H_4·CHEt·)$_2$] described above have the same configuration (cf. Carlisle *et al.*, A., 1941, I, 103) as (**II**). H. B.

4-Arylamino-2-alkenylphenols.—See B., 1942, II, 218.

Organic thiocyano-compounds. H. P. Kaufmann (*Angew. Chem.*, 1941, **54**, 168—169).—A literature survey. A. T. P.

4-Amino-4'-hydroxydiphenyl sulphone and derivatives.—See B., 1942, III, 157.

***m*-Cresolsulphonic acids and their separation.** A. Tschitschibabin and C. Barkovsky (*Compt rend.*, 1941, **213**, 206—209).—*m*-Cresol (**I**) and H_2SO_4 at 120° afford 3 : 1 : 6- (**II**) and 3 : 1 : 4-OH·C_6H_3Me·SO_3H (Ba salt, decomp. slowly >200°), and some disulphonic acid (**III**) (*salt*, ? $C_7H_5O_7S_2Ba_{1\cdot5}$,10H_2O, described). (**I**) and $ClSO_3H$ give (**II**), (**III**), and some " α-*m*-cresolsulphone " (cf. Haworth *et al.*, A., 1924, i, 848; Zehenter *et al.*, A., 1929, 692). A. T. P.

Hydrogenation of phenyl alkyl ketones in presence of copper–alumina catalysts. V. N. Ipatieff and V. Haensel (*J. Amer. Chem. Soc.*, 1942, **64**, 520—521).—Prep. of active CuO–Al_2O_3 catalysts from the nitrates is described. In presence of CuO, hydrogenation of COPhMe does not occur at <260°/164 atm., but in presence of 99 : 1 CuO–Al_2O_3 is rapid at 115°/117 atm., yielding pure CHPhMe·OH. The best catalysts are CuO + 2·5—8% of Al_2O_3. In presence of 96 : 4 CuO–Al_2O_3 at 115—116°/100 atm., times for complete hydrogenation of COPhR (50 c.c. in *cyclo*hexane) to CHPhR·OH are R = Me 29, Et 37, Pr$^\alpha$ 286, Bu$^\alpha$ 138, *n*-amyl 25, *n*-heptyl 19, and *n*-nonyl 14 min.; at 150—180° 95—98% of CH_2PhR is obtained. α-*Phenyl*-n-*propyl*, b.p. 93°/4 mm., -*amyl*, b.p. 115°/6 mm., -*hexyl*, b.p. 128°/5 mm., and -*octyl*, b.p. 140°/8 mm., *alcohol* are incidentally described. R. S. C.

Dehydration of α-phenyl-β-methyl-β-propenyl[-ethylene] glycol; dehalogenation of its iodohydrin and isomerisation of the corresponding oxide. Y. Deux (*Compt. rend.*, 1941, **213**, 209—211; cf. A., 1939, II, 420).—OH·CHPh·CMe(OH)·CH:CHMe, m.p. 125—126°, and 30% H_2SO_4 at 110° afford (migration of Ph) CHMe:CH·CPhMe·CHO (**I**), b.p. 120°/16 mm. (semicarbazone, m.p. 135—136°), hydrogenated (Raney Ni) to CPhMePr$^\alpha$·CHO, b.p. 101—102°/16 mm. (semicarbazone, m.p. 190°). α-Phenyl-β-methyl-Δ$^{\alpha\gamma}$-pentadiene (**II**), b.p. 112—113°/15 mm., affords a chlorohydrin (*p*-nitrobenzoate, m.p. 94—95°), and thence (powdered KOH) αβ-oxido-α-phenyl-β-methyl-Δ$^\gamma$-pentene, b.p. 117—118°/16 mm. [hydrogenated to CHMePr$^\alpha$·CHPh·OH (*p*-nitrobenzoate, m.p. 65°), also obtained from PhCHO and CHMePr$^\alpha$·MgCl], which is isomerised at 250—300° (kieselguhr) or by $MgBr_2$–Et_2O (cold) to (**I**). (**II**) and HgO–I in Et_2O–H_2O, followed by $AgNO_3$, yield γ-phenyl-Δ$^{\gamma \text{ or } \delta}$-hexen-β-one, catalytically reduced to γ-phenylhexan-β-one (semicarbazone, m.p. 130°). A. T. P.

2 : 2'-Dihydroxy-5 : 5'-dimethyl-3-hydroxymethyldiphenylmethane. P. Maitland and D. C. Pepper (*J.S.C.I.*, 1942, **61**, 66).—CH_2(C_6H_3Me·OH-5 : 2)$_2$, paraformaldehyde, and 5% aq. NaOH at room temp. give the 3 : 3'-di(hydroxymethyl) derivative (**I**), m.p. 147°, and the OH·CH_2 derivative (**II**), m.p. 148°, which with 30% CH_2O and 2% aq. NaOH affords (**I**). The substance of m.p. 99—100° described by Megson *et al.* (*Nature*, 1937, **140**, 642) cannot be (**II**). W. C. J. R.

Synthesis of polyenic carotenoid analogues. V. V. Schokina, O. V. Kildischeva, and N. A. Preobrashenski (*J. Gen. Chem. Russ.*, 1941, **11**, 425—428).—αθ-*Di*-(2 : 2 : 6-*trimethyl*-Δ^6-cyclo*hexenyl*)-γζ-*dimethyl*-Δ$^{\alpha\eta}$-*octadien*-Δ$^\delta$-*inene*-γζ-*diol*, m.p. 106—110° (decomp.), was prepared from β-ionone (**I**) and (ClC·MgBr)$_2$ (**II**). αβ-*Di*-(1-*hydroxy*-2- and -3-*methyl*cyclo*hexyl*)*acetylene*, m.p. 111—113° and 104°, respectively, are similarly obtained from (**II**) and 2- and 3-methylcyclohexanone, respectively. The condensation of mono- into di-acetylenic compounds was carried out by the methods of Nieuwland *et al.* (A., 1932, 40) and Salkind *et al.* (A., 1939, II, 531 etc.). ακ-*Di*-(2 : 2 : 6-*trimethyl*-Δ^6-cyclo*hexenyl*)-γθ-*dimethyl*-Δ$^{\alpha\iota}$-*decadiene*-Δ$^{\delta\zeta}$-*di-inene*-γθ-*diol*, m.p. 109—111° (decomp.), was prepared by condensing 2 mols. of the condensation product of C_2H_2 and (**I**). N. G.

Quantum mechanical calculations on the theory of organic dyes.—See A., 1942, I. 229.

Synthetic mydriatics. I. F. F. Blicke and C. E. Maxwell (*J. Amer. Chem. Soc.*, 1942, **64**, 428—431).—Many benzilates are mydriatics, notably the β-diethylamino- and β-piperidino-ethyl esters. Quaternary salts are as active as hydrochlorides and often more sol. Five ketones, COPh·[CH_2]$_n$·NRR' (*n* = 1 or 2), have little, if any, mydriatic activity. *I*, *S*, and *A* below denote inactivity, slight, and great activity, respectively, as mydriatics. The following are recorded. β-Diethylamino- (hydrochloride, m.p. 135—136°), β-di*cyclo*hexylamino- [prep. from NH(C_6H_{13})$_2$ by OH·[CH_2]$_2$·Cl at 150°], b.p. 165—167°/6 mm., β-*N*-methylanilino- (similarly prepared), b.p. 151—153°/15 mm., β-piperidino- (similarly prepared), b.p. 196—199], β-morpholino-, b.p. 220—222°, β-*cyclo*hexylamino- (**I**) (prep. with *cyclo*hexyldi-β-hydroxyethylamine, b.p. 175—178°/12 mm., from *cyclo*hexylamine), b.p. 127—130°/15 mm., β-*N*-*cyclo*hexyl-*N*-methylamino- [prep. from (**I**) by CH_2O–NaOH at 100°], b.p. 115—116°/13 mm., -ethyl alcohol; α-piperidinopropan-β-ol, b.p. 191—194°; β-diethylamino- (hydrochloride, m.p. 210—211°), β-*dibutylamino*-, b.p. 114—115°/23 mm., β-N-cyclo*hexyl*-N-*methylamino*-, b.p. 99—100°/11 mm., β-di*cyclo*hexylamino- (hydrochloride, m.p. 185—186°), β-*N*-methylanilino-, b.p. 126—128°/8 mm., β-piperidino- (hydrochloride, m.p. 229—231°), and β-morpholino-, b.p. 104—106°/29 mm., -ethyl chloride; 1-γ-phenoxy-*n*-propylpiperidine, b.p. 152—154°/5 mm., and thence (48% HBr) γ-piperidino-*n*-propyl bromide hydrobromide, m.p. 210—211°; β-chloro-α-piperidinopropane hydrochloride, m.p. 203—204°. Horenstein and Pählicke's method (A., 1938, II, 396) yields : β-*amino*-, m.p. 170—171°, β-butylamino- [*hydrochloride* (*I*), m.p. 121—122°], β-diethylamino- [hydrochloride (*A*), m.p. 174—175°; *methobromide* (*A*), m.p. 169—170°], β-dibutylamino- [*hydrochloride* (*I*), m.p. 126—127°; *methobromide* (*I*), m.p. 138—139°], β-*N*-*cyclo*hexyl-*N*-methylamino- [*hydrochloride*, m.p. 154—155°; *methobromide* (*S*), m.p. 153—154°], β-di*cyclo*hexylamino- [*hydrochloride* (*I*), m.p. 197—198°], β-N-*methylanilino*-, m.p. 78—79° [*methobromide* (*I*), m.p. 179—180°], β-morpholino- [*hydrochloride* (*S*), m.p. 180—181°; *methobromide* (*S*), m.p. 203—204°], and β-piperidino- [*hydrochloride* (*A*), m.p. 175—176°; *methobromide* (*A*), m.p. 202—203°], -ethyl benzilate; γ-piperidino-*n*-propyl [*hydrobromide* (*A*), m.p. 168—169°; *methobromide* (*A*), m.p. 168—169°], β-piperidino*iso*propyl [*hydrochloride*, m.p. 167—168°; *methobromide* (*I*), m.p. 176—177°], and γ-piperidino-ββ-dimethyl-*n*-propyl benzilate [*hydrochloride* (*S*), m.p. 170—171°]. COMeAr, $(CH_2O)_x$, and NHR_2,HCl in boiling abs. EtOH give *Ph di-β-isoamylamino*-(*I*) (36·8%), m.p. 269—270°, β-$C_{10}H_7$, β-*dimethylamino*- (69%), m.p.

153—154°, and *β-C*$_{10}H_7$ *β-piperidino-* (60%), m.p. 240—241°, *-ethyl ketone hydrochloride*; the last is hydrogenated (Raney Ni; H_2O; 3 atm.) to the corresponding *carbinol hydrochloride*, m.p. 191—192°. Ph β-piperidinoethyl ketone and 2% Na–Hg in dil. HCl give (?) αζ-dipiperidino-γδ-diphenyl-*n*-hexane-γδ-diol, m.p. 236—237°. R. S. C.

Specific rotation of *l*-tyrosine. W. H. Stein, S. Moore, and M. Bergmann (*J. Amer. Chem. Soc.*, 1942, **64**, 724—725).—Prep. by six methods gives *l*-tyrosine, $[\alpha]_D^{20}$ −10·3°, $[\alpha]_D^{20}$ −11·8°, $[\alpha]_D^{16}$ −13·0° in 4% HCl, $[\alpha]_D^{20}$ −7·0°, $[\alpha]_D^{20}$ −8·5°, $[\alpha]_D^{16}$ −9·6° in 20% HCl (temp. ±0·3°; [α] ±0·2°) (cf. lit. various, −8·64° to −16·2°). R. S. C.

Crotonic acid series. II. Nitrogen derivatives of α-phenylcrotonic acid. M. A. Phillips (*J.C.S.*, 1942, 220—223; cf. A., 1927, 132).—CHPhEt·COCl (I) and dry Br at 50° afford *α-bromo-α-phenylbutyryl bromide* (II), b.p. 150—154°/22 mm., converted by EtOH at 60°, then at the b.p., into CHMe:CPh·CO_2Et, b.p. 123—124°/10 mm. (contains 0·5% of Br), and thence (boiling aq. KOH–EtOH) CHMe:CPh·CO_2H, stable form (III), m.p. 136° [*chloride* (IV), b.p. 131°/10 mm.]. (II) and aq. NH_3 (*d* 0·88) at 40° yield CHMe:CPh·CO·NH_2, stable form, m.p. 104°, also obtained from (IV) (cf. Pfeiffer *et al.*, A., 1929, 184). (II) and $CO(NH_2)_2$ at 55° yield a product, m.p. 167°, containing 2·3% of Br, and thence (1% aq. NaOH at 50°) *α-phenylcrotonylcarbamide* (labile form), m.p. 197°, and some (III). (IV) and $CO(NH_2)_2$ at 30° afford *α-phenylcrotonylcarbamide* (stable form), m.p. 185°; both stable and labile forms are converted by aq. NaOH into (III). Reduction of either form with 4% Na–Hg yields α-phenylbutyrylcarbamide (V), m.p. 147°, also obtained from (I) and $CO(NH_2)_2$ at 30°. (I) and $CO(NH_2)_2$ at 90° afford *NN'-di-(α-phenylbutyryl)carbamide*, m.p. 172°, hydrolysed by aq. NaOH–EtOH at 90° to CHPhEt·CO_2H. (V) in H_2O with Br at 20° gives α-(o- or p-*bromophenyl*)-*butyrylcarbamide* (VI), m.p. 178—179°, hydrolysed by aq. KOH–EtOH to the *-butyric acid*, m.p. 40—43°. Tests on mice indicate that (VI) has about half the hypnotic activity of α-bromo-α-ethylbutyrylcarbamide, and is more toxic. A. T. P.

Effect of substituents at the olefinic carbon atoms on physicochemical properties of chromophoric vinylene and divinylene groups. —See A., 1942, I, 225.

"*trans*"-2 : 2 : 6-Trimethyl*cyclo*hexanecarboxylic acid : a second solid naphthenic acid from Californian petroleum. B. Shive, J. Horeczy, G. Wash, and H. L. Lochte (*J. Amer. Chem. Soc.*, 1942, **64**, 385—391).—The acids (70 l.) from Californian petroleum yield an acid (I), $C_{10}H_{18}O_2$ (1800 g.), m.p. 83° (also camphonanic and liquid acids), identical with that obtained (Shive *et al.*) by degradation of a base, $C_{16}H_{25}N$, from the same source and with Kennedy's acid (B., 1940, 9) from Persian petroleum. It is shown by synthesis to be (? trans-)2 : 2 : 6-*trimethyl*cyclo*hexanecarboxylic acid*. It could not be esterified directly, but the acid chloride (II) (prep. by $SOCl_2$, first at room temp. and then at the b.p.), b.p. 218·5°/747 mm., yields the Me ester, b.p. 210°/747 mm., which is unaffected by KOH–aq. EtOH, conc. aq. NH_3 at 125°, or H_2–Cu chromite at 250°/4000 lb. (*n*-C_5H_{11}·CO_2Et gives thus quantitatively *n*-C_6H_{13}·OH). At 110° (I), 1 : 2 : 2-trimethyl*cyclo*pentane- and *cyclo*hexane-carboxylic acid give 52, 90, and 19% of CO and 0·15, 0·05, and 1·00% of CO_2, respectively, indicating erroneously that (I) is a *tert.* acid (cf. Whitmore *et al.*, A., 1938, II, 427). The *ethylamide* [from (II) by NH_2Et–C_6H_6 at room temp.], m.p. 126°, of (I) with PCl_5 in boiling C_6H_6 gives an impure product, b.p. 96°/8 mm., hydrolysed by boiling H_2O to a *Cl-amide*, $C_{12}H_{22}ONCl$, m.p. 84° (yields unsaturated acids and no Cl-acid), whence the Cl no. (von Braun *et al.*, A., 1927, 547) is calc. to be 120, indicating a *sec.* acid. With HN_3, (I) gives the amine (III), C_9H_{17}·NH_2 (picrate, m.p. 226—227°; *Ac* derivative, m.p. 133—134°), of Roberts *et al.*, which with aq. CH_2O–HCO_2H at 120° gives the *NN*-Me_2 derivative (IV), b.p. 204—205°/746 mm. (*picrate*, m.p. 262—263°). This yields a methiodide, m.p. 272—273°, and thence a methohydroxide, which regenerates (IV) when distilled in steam. With $NaNO_2$ in aq. AcOH at 0°, (III) gives, by ring-contraction, 1-*methyl*-2-iso*propenyl*cyclo*pentane*, b.p. 140°/750 mm. (and some alcohol), which with O_3 in CCl_4 yields 2-acetyl-1-methyl*cyclo*pentane (V) (semicarbazone, m.p. 160—161°). Distillation of the phosphate of (III) gives hydrocarbons, C_9H_{16}, b.p. 142·5—150·5°/754 mm. [and some (III)], converted by O_3 into a $(CO)_2$-compound (disemicarbazone, m.p. 206°) and acids, but not (V) or $COMe_2$. *α-cyclo*Geranic acid with H_2–PtO_2 in AcOH gives (? cis-)2 : 2 : 6-*trimethyl*cyclo*hexanecarboxylic acid* (VI), m.p. 74—75°, but with H_2–Pd–$BaSO_4$–AcOH gives a mixture, m.p. 39—43°, of isomerides. A little conc. HCl in AcOH at 180—190° rearranges (VI) to (I), which, by way of (II), yields the *anilide* (VII), m.p. 191—192° [with $SOCl_2$ and then NH_2Ph–Et_2O, (VI) gives a mixture whence only (VII) is isolable and is thus partly isomerised by $SOCl_2$], amide, m.p. 191°, *p-toluidide*, m.p. 193°, *p*-bromoanilide, m.p. 216°, Et, b.p. 225°/747 mm., and Ph ester, b.p. 275°/750 mm., and *nitrile*, b.p. 221—222°/748 mm. R. S. C.

Catalytic oxidation of alkyl-substituted aromatic compounds.—See B., 1942, II, 219.

Halogenophenolcarboxylic acids.—See B., 1942, III, 157.

Compounds of naphthoic acids with their copper and nickel salts. Copper and nickel sulphinates and their oxidation to sulphonates. (Mrs.) W. G. Wright (*J.C.S.*, 1942, 263—266; cf. A., 1940, II, 303).—*p*-C_6H_4Me·SO_2H and $CuCO_3$–EtOH give (from H_2O) (*p*-C_6H_4·SO_2)$_2$Cu,3H_2O, 2 forms [also +0·5H_2O (from cold solution)]. (*p*-C_6H_4Me·SO_3)$_2$Cu,6H_2O loses 4H_2O at 100° forming a white powder, and at 240° it loses 6H_2O to give a green powder. (2-$C_{10}H_7$·SO_2)$_2$Cu,6H_2O similarly loses 4H_2O at 100°, but the corresponding Ni salt loses no wt. at 100°. (1-$C_{10}H_7$·SO_3)$_2$Cu,6H_2O loses 2H_2O at 100°, and 6H_2O at 185°, and the Ni salt loses 3H_2O at 100°, 4H_2O at 150°, and 6H_2O at 185°. The colour changes accompanying dehydration are recorded. α-$C_{10}H_7$·CO_2H (I) and $NiCO_3$ in EtOH afford *Ni α-naphthoate* (II), +4H_2O (from H_2O) (sol. in org. solvents); a similar reaction for 6 months gives (II) and the *acid salt* (*A*), Ni($C_{11}H_8O_2$)$_2$,$C_{11}H_9O_2$,2H_2O, m.p. 135° (decomp.) [very sol. in org. solvents; when heated affords (I)]. *Ni β-naphthoate*, +3H_2O, is decomposed by C_6H_6, Et_2O, or $CHCl_3$, and repeated treatment with $COMe_2$ affords the *acid salt* [as (*A*)], m.p. 148° (decomp.), and *basic salt*, 3Ni($C_{11}H_8O_2$)$_2$.Ni(OH)$_2$. (I) and $CuCO_3$–Cu(OH)$_2$ in EtOH (boiled for 5 min. and then kept for 1 week) yield *Cu α-naphthoate*, +EtOH (dark green), converted by $COMe_2$ into ($C_{11}H_7O_2$)$_2$*Cu*,*COMe*$_2$, which is decomposed in Et_2O, $CHCl_3$, C_6H_6, CCl_4, or EtOH to the *basic salt*, ($C_{11}H_7O_2$)$_2$Cu,Cu(OH)$_2$, also formed from the normal salt and boiling EtOH. *Cu β-naphthoate* (II) and $COMe_2$ at 35°, kept without evaporation at 12° for 12 hr., yield the *acid salt*, 3($C_{11}H_7O_2$)$_2$Cu,$C_{11}H_8O_2$; (II) and boiling $COMe_2$ give the *basic salt*, ($C_{11}H_7O_2$)$_2$Cu,Cu(OH)$_2$. *p*-C_6H_4Me·SO_2H and $NiCO_3$–EtOH (1 week) give *Ni* p-*toluenesulphinate* (cream; insol. in EtOH), oxidised in EtOH suspension by air to the *sulphonate*, +6H_2O (loses 4H_2O at 100° and 6H_2O at 180°). *Cu* 1-*naphthalenesulphinate* (yellow), from 1-$C_{10}H_7$·SO_2H and $CuCO_3$ in boiling EtOH or Et_2O, separates from a saturated aq. solution at 0° as the *hexahydrate* (pale blue) (Cu ion may be surrounded with H_2O mols.). 1-$C_{10}H_7$·SO_2H and $NiCO_3$ yield some *Ni* 1-*naphthalenesulphinate*, +2H_2O (cream) (formed in Et_2O; the sulphonate is obtained in EtOH), or +4H_2O (green) (from H_2O). *Cu* (anhyd., yellow; +2H_2O, green) and *Ni* 2-*naphthalenesulphinate* are oxidised in EtOH–C_6H_6 by air to the corresponding *sulphonates* in 50% yield. The Cu salts may be used for identification of 1- and 2-$C_{10}H_7$·SO_2H. A. T. P.

Aminohydroxynaphthoic acids. I. V. Hopper, A. C. Syme, and F. J. Wilson (*J. Soc. Dyers and Col.*, 1942, **58**, 93—97).—2 : 7-OH·$C_{10}H_6$·NH_2 and -$C_{10}H_6$(NH_2)$_2$ could not be converted (diazo-reaction; diazotisation with NO·SO_4H in AcOH or, better H_3PO_4) into the corresponding nitrile. 2 : 7-NH_2·$C_{10}H_6$·SO_3Na (I) (dehydrated at 70°/10 mm.) [*Bz* derivative (+4H_2O)] and $K_4Fe(CN)_6$, distilled at 5 mm. in N_2, give some 2 : 7-NH_2·$C_{10}H_6$·CN, new m.p. 192—195°, whereas (I)–KCN (+ a little C_6H_6) at 400—420° (sealed tube; in air or N_2) yield β-$C_{10}H_7$·NH_2. (I) yields a diazo-compound (modified prep.), which with CuCN–HCl, followed by hydrolysis with aq. NaOH, yields 2 : 7-SO_3H·$C_{10}H_6$·CO_2H, and thence 2 : 7-OH·$C_{10}H_6$·CO_2H, new m.p. 273—274°, and -NH_2·$C_{10}H_6$·CO_2H [Ac derivative, m.p. 287—288° (lit. 200—201°)]. 2 : 7-NHAc·$C_{10}H_6$·CO_2Na and 22% oleum at 40—45° afford a partially hydrolysed product, converted by aq. NaOH into *sulpho-2-amino-7-naphthoic acid*, +H_2O (II). Diazotisation (NO·SO_4H–H_3PO_4) of (II) followed by NaH_2PO_2–HCl at 80° gives mixed SO_3H·$C_{10}H_6$·CO_2H, converted by KOH fusion into mixed OH·$C_{10}H_6$·CO_2H, m.p. 210—220°. Attempted separation of (II) through a *Ba* salt (+2H_2O) (*salt* +3H_2O, described also), followed by fusion with KOH, also gives mixed OH·$C_{10}H_6$·CO_2H. 1-*Benzeneazo*-2-*hydroxy*-6-, m.p. 283—285°, and -7-*naphthoic acid*, m.p. 273—275°, are reduced by anhyd. $SnCl_2$–AcOH to 1-amino-2-hydroxy-6- and -7-naphthoic acid (isolated as *hydrochlorides*), respectively, which oxidise rapidly in air. A. T. P.

αα-Diphenylglutaric acid. F. Salmon-Legagneur (*Compt. rend.*, 1941, **213**, 182—184).—CNPh$_2$·CN and CH_2Br·CH_2·CO_2Et give 60—65% of the *Et* ester (I), m.p. 61°, of *γ-cyano-γγ-diphenyl*-n-*butyric acid*, m.p. 156—157°. Dissolution of the acid in 80% H_2SO_4 and pptn. by H_2O yields *αα-diphenylglutarimide* (II), m.p. 158—159°, hydrolysed (dil. NaOH) to *γ-carbamyl-γγ-diphenyl*-n-*butyric acid* (III), m.p. 142—144°, and thence (boiling conc. NaOH) to *αα-diphenylglutaric acid* (IV), m.p. 183° [*anhydride* (prep. by AcCl), m.p. 138—139°]. (I) with 80% H_2SO_4 yields (II) and the *Et* ester, m.p. 143—145°, of (III); the mixture is hydrolysed by alkali to (IV) (yield comparable with that by other route). Direct esterification of (IV) affords *Me*, m.p. 108°, and *Et*, m.p. 120—121°, *γ-carboxy-γγ-diphenyl*-n-*butyrate*, whereas alkali salts of (IV) and Alk_2SO_4 give the Me_2, m.p. 64—65°, and Et_2, oily, esters, which are hydrolysed to *γ-carbomethoxy-*, m.p. 129°, and *γ-carbethoxy-*, m.p. 107°, *-γγ-diphenyl*-n-*butyric acid*, respectively. C. S.

3 : 4-Dihydronaphthalene-1 : 2-dicarboxylic acid.—See B., 1942, II, 219.

Oxidation and determination of the mol. wt. of polynuclear aromatic compounds. W. P. Campbell, M. D. Soffer, and T. R. Steadman (*J. Amer. Chem. Soc.*, 1942, **64**, 425—428).—When polycyclic hydrocarbons are oxidised by 1 : 2 conc. HNO_3–H_2O at 190—200°, the more highly substituted ring usually survives (cf. A., 1940, II, 279).

Thus, 1 : 6 : 7 : 4-$C_{10}H_4Me_3Pr^{\beta}$ gives 1 : 2 : 4 : 5-$C_6H_2(CO_2H)_4$ (I); 1 : 3 : 6 : 7 : 4-$C_{10}H_3Me_4Pr^{\beta}$ gives $C_6H(CO_2H)_5$. 1 : 2 : 6 : 7 : 4-$C_{10}H_3Me_4Pr^{\beta}$ with CrO_3 and then HNO_3 gives (I). 3-Acetoxyretene with $AlCl_3$–AcCl in $PhNO_2$ at 0° and later room temp. gives 3-*acetoxy*-9(? 10)-*acetylretene* (II), m.p. 169—170°, oxidised by HNO_3 to $C_6H(CO_2H)_5$ and hydrolysed by alkali to 9(? 10)-acetyl-3-retenol, m.p. 247—248° (corr.), which with Me_2SO_4–NaOH in 50% aq. MeOH gives the *Me ether*, m.p. 133—133·5° (corr.), also obtained from 3-methoxyretene by $AlCl_3$–AcCl–$PhNO_2$. The mol. wt. of a polyalkylnaphthalene is readily and accurately (±1%) determined by titrating the picrates with 0·05N-NaOH (phenolphthalein) in H_2O–C_6H_6 (1 : 10 by vol.). R. S. C.

Synthesis of phthalaldehydes. T. C. Chaudhuri (*J. Amer. Chem. Soc.*, 1942, **64**, 315).—PhCHO (10 c.c.), $CHCl_3$ (8 c.c.), KOH (30 g.), and H_2O (50 c.c.) at 140—150° give m-, b.p. 192—196° (odour of rose; irritant), and less (22%) o-*dichloromethylbenzaldehyde*, b.p. 170—175°, hydrolysed to *m*- and *o*-$C_6H_4(CHO)_2$, respectively. R. S. C.

Friedel–Crafts reaction in sulphur dioxide.—See B., 1942, II, 216

Comparison of metallic chlorides as catalysts for the Friedel–Crafts ketone synthesis. II. O. C. Dermer and R. A. Billmeier (*J. Amer. Chem. Soc.*, 1942, **64**, 464—465).—Yields of COPhMe obtained after 1—9 or 1—24 hr. by the Perrier technique (A., 1900, i, 331) at 20—25° using various catalysts are recorded. These conditions improve the yield for catalysts previously found (A., 1942, II, 143) good, but lower it for mediocre or poor catalysts; yields at 80—110° are intermediate. BzCl combines with Ph_2O in absence of $HgCl_2$, but less well than in its presence. R. S. C.

Nitrosation of aryl alkyl ketones.—See B., 1942, II, 219.

Keten acetals. VIII. Reaction of keten diethyl acetal with αβ-unsaturated carbonyl compounds. S. M. McElvain and H. Cohen (*J. Amer. Chem. Soc.*, 1942, **64**, 260—265; cf. A., 1942, II, 216).—$CH_2{:}C(OEt)_2$ (I) (4 mols.) and $(CH{\cdot}CO)_2O$ (II) (1 mol.) in Et_2O give rapidly 3 : 5-*diethoxy*-1 : 6-*dihydrophthalic anhydride* (III) (71%), m.p. 110—111°, by way of the 3 : 3 : 6 : 6-tetraethoxyhexahydroanhydride. After several days in C_6H_6, (I) (2 mols.) and (II) (1 mol.) give 1 : 5-*diethoxy*-3 : 4 : 7 : 8-*tetracarboxy*dicyclo[2, 2, 2]-Δ^5-*octene dianhydride*, m.p. 253—255°, best prepared from (III) and (II) in hot C_6H_6. With Pd in boiling xylene, (III) gives 3 : 5 : 1 : 2-$(OEt)_2C_6H_2(CO)_2O$ (derived N-*phenylimide*, m.p. 167—168°). H_2O readily hydrolyses (III), causing also loss of EtOH and yielding 3-*keto*-5-*ethoxy*-Δ^4-*tetrahydrophthalic acid*, which at the m.p. (83—85°) gives 3-*keto*-5-*ethoxy*-Δ^4-*tetrahydrobenzoic acid*, m.p. 124—125°. In boiling EtOH, (III) gives 3-*keto*-5-*ethoxy*-2-*carbethoxy*-Δ^4-*tetrahydrobenzoic acid* (43%), m.p. 148—149°, stable to heat. With $(CH{\cdot}CO_2Et)_2$ at 195°, (I) gives (after hydrolysis) a little 3 : 5 : 1 : 2-$(OEt)_2C_6H_2(CO_2H)_2$ with much polymerisation and pyrolysis. $(CMe{\cdot}CO)_2O$ does not react with (I) in C_6H_6 and at 175—180° gives an inseparable mixture. *p*-$O{:}C_6H_4{:}O$ and (I) alone at ~80° violently or in boiling C_6H_6 smoothly give 2 : 5-*diketo*-7-*ethoxy*dicyclo[4, 2, 0]-$\Delta^{3:6}$-*octadiene*, $\begin{matrix}CH{\cdot}CO{\cdot}CH{\cdot}CH_2\\ |\\ CH{\cdot}CO{\cdot}C{=}C{\cdot}OEt'\end{matrix}$, m.p. 94—95°, converted by boiling dil. HCl into 2 : 5 : 1-$(OH)_2C_6H_3{\cdot}CH_2{\cdot}CO_2H$ (*Me* ester, m.p. 116—117°). $CO(CH{:}CHPh)_2$ and (I) at the b.p. give 2-*cinnamoyl*-1 : 1-*diethoxy*-3-*phenyl*cyclo*butane*, m.p. 87—88°, hydrolysed by boiling HCl–H_2O–dioxan to $CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$, m.p. 157—158°, and converted by Br–CCl_4 into *Et* γ-*bromo*-δ-*keto*-βζ-*diphenyl*-Δ^{ϵ}-*heptenoate*, m.p. 111—112° (*dibromide*, m.p. 171—172°). $COPh{\cdot}CH{:}CHPh$ and (I) at the b.p. give 2-*benzoyl*-1 : 1-*diethoxy*-3-*phenyl*cyclo*butane*, b.p. 168—170°/0·5 mm., hydrolysed to $CH_2Bz{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$. Phorone and $COMe{\cdot}CH{:}CHPh$ do not condense with (I), polymerisation and self-condensation occuring in the latter case. R. S. C.

Naphthenic acid. I. Synthesis of 3 : 3 : 4-trimethyl*cyclo*pentanone. E. R. Buchman and H. Sargent (*J. Org. Chem.*, 1942, **7**, 148—153).—3 : 3 : 4-*Trimethyl*cyclo*pentanone* (I) is not identical with the $C_8H_{14}O$ ketone obtained by von Braun from naphthenic acids and consequently the formulation of certain naphthenic acids as related to this ketone is in error. 3 : 4 : 4-Trimethyl*cyclo*hexanone (II) in AcOH at 0° is converted by Br into the 6 : 6-*Br*$_2$-compound, m.p. 81·2—81·7°, transformed by aq. KOH into 4 : 4 : 5-*trimethyl*cyclo*hexane*-1 : 2-*dione*, m.p. 93·5—94·1°. This is oxidised by H_2O_2 in alkaline solution to *ββγ-trimethyladipic acid*, m.p. 127·3—127·6°, which is transformed by $MnCO_3$ at 280—320° into (I), b.p. 172—173° (corr.)/742 mm. (*semicarbazone*, m.p. 213·5—214°; *oxime*, m.p. 99·8—100°; p-*nitrobenzylidene* derivative, α-form, orange-yellow needles, m.p. 204·7—205·1°, β-variety, paler rhombs, m.p. 202·0—202·5°). Successive treatments with Br and NaOH transform (II) into 1-*hydroxy*-3 : 3 : 4-*trimethyl*cyclo*pentane*-1-*carboxylic acid*, two forms, m.p. 114·0—114·5° and 109—110°, oxidised ($KMnO_4$) to (I). H. W.

Synthesis of 3:3:4-trimethyl*cyclo*pentanone. II. H. Sargent (*J. Org. Chem.*, 1942, **7**, 154—157).—$CMe_2{:}CHMe$ is converted into its nitrosate, which is condensed with $CHAcNa{\cdot}CO_2Me$ to $CO_2Me{\cdot}CHAc{\cdot}CMe_2{\cdot}CMe{:}N{\cdot}OH$, m.p. 148·5—149·0°. This with boiling 50% KOH gives a mixture of 3 : 4 : 4-*trimethyl*-Δ^2-cyclo*pentenone* (I), b.p. 87·5—88·0°/20 mm. (non-cryst. oxime; *semicarbazone*, m.p. 199·5—200°), which does not afford a compound with $NaHSO_3$, and 3 : 5 : 5-*trimethyl*-Δ^2-cyclo*pentenone* (II), b.p. 76·5—77·0°/mm. (*oxime*, m.p. 108—108·2°; *semicarbazone*, m.p. 205·0—205·5°), which does not unite with $NaHSO_3$. (I) is catalytically reduced to 3 : 3 : 4-trimethyl*cyclo*pentanone, b.p. 173—175° (corr.)/742 mm. [oxime, m.p. 100·8—101·0° (corr.)], which reacts slowly with saturated aq. $NaHSO_3$. Similarly (II) affords 2 : 2 : 4-*trimethyl*cyclo*pentanone*, b.p. 153—154°/742 mm. (*semicarbazone*, m.p. 171·0—171·3°; *oxime*, m.p. 79·7—80°; p-*nitrobenzylidene* derivative, m.p. 99·3—99·5°), which does not unite with $NaHSO_3$. H. W.

Tiemann's "*iso*camphorphorone." E. R. Buchman and H. Sargent (*J. Org. Chem.*, 1942, **7**, 140—147).—Tiemann's "*iso*camphorphorone" is a mixture of 3 : 6 : 6- (I) and 3 : 4 : 4-*trimethyl*-Δ^2-cyclo*hexenone* (II). β-Campholenic acid is oxidised in accordance with Tiemann's directions or, more conveniently, NH_4 β-campholenate is oxidised by $KMnO_4$ to dihydroxydihydro-β-campholenolactone (III), m.p. 143·6—144·6° (corr.), and $CMe_2Ac{\cdot}[CH_2]_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$ (IV). (III) is completely converted into (IV) by subsequent use of $Pb(OAc)_4$, after which the reaction mixture is acidified with H_2SO_4 and steam-distilled, thus giving (II), b.p. 98°/13 mm. (*semicarbazone*, m.p. 206·5—207°; *oxime*, m.p. 53·8—54·5°), and (I), b.p. 86°/13 mm. (semicarbazone, m.p. 201·0—201·1°; 3-hydroxylamino-3 : 6 : 6-trimethyl*cyclo*hexanoneoxime, m.p. 156·5—157°). (I) and (II) do not react with aq. $NaHSO_3$. Oxidation ($KMnO_4$) of (II) leads to δ-keto-γγ-dimethylhexoic acid or to (?) 3 : 4 : 4-trimethyl*cyclo*hexane-1 : 2-dione, m.p. 39·0—39·5° (*semicarbazone*, m.p. 189—190°), if less oxidant is used. (II) is readily hydrogenated (Pd–C in MeOH) to 3 : 4 : 4-*trimethyl*cyclo*hexanone*, b.p. 80—81°/13 mm. (cryst. $NaHSO_3$ compound; *semicarbazone*, m.p. 208—209°; *oxime*, m.p. 72·5—73·5°; *di*-p-*nitrobenzylidene* derivative, m.p. 223·0—223·2°). (I) is similarly reduced to pulenone, b.p. 66—67°/13 mm. (semicarbazone, m.p. 176·0—176·3°; oxime, m.p. 94·5—94·8°; *mono*-p-*nitrobenzylidene* derivative, m.p. 117·5—118·0°). Oxidation of (III) by $Pb(OAc)_4$ in AcOH affords (after steam-distillation etc.) (II) in 52% yield. β-Campholenic acid or its NH_4 salt is oxidised by 30% H_2O_2 in AcOH to hydroxydihydro-β-campholenolactone, m.p. 143·0—143·5°, which does not appear to be oxidised further by $Pb(OAc)_4$ or CrO_3. With HCl–EtOH it yields a *substance*, b.p. 104—106°/2 mm., which does not react with $Pb(OAc)_4$ and does not regenerate the lactone when hydrolysed by alkali. H. W.

Oxidation product of $\Delta^{9:10}$-octahydronaphthalene. G. C. Harris (*J. Amer. Chem. Soc.*, 1942, **64**, 720).—The 1-keto-octahydronaphthalene obtained by SeO_2 (A., 1942, II, 90) with MgMeCl gives an unsaturated (Br) substance but no 1 : 4 addition (to yield a ketone) and is thus probably the $\Delta^{9:10}$-compound (cf. Woodward, A., 1942, II, 161, 164). R. S. C.

Reaction of Grignard reagent with acyloxyanthrones. L. F. Fieser and H. Heymann (*J. Amer. Chem. Soc.*, 1942, **64**, 376—382).—*p*-$C_6H_4Me{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2Na$-*o* in H_2O with H_2–Cu chromite at 200°/1500—2000 lb. gives *p*-$C_6H_4Me{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$ (65%), m.p. 133·6—135·8°, cyclised by HF to 2-methylanthr-9-one, m.p. 102·3—103·8°, which yields 10-bromo- (92·8%), decomp. 133° (bath preheated at 125°), and thence (AgOAc–AcOH) 10-acetoxy-2-methylanthr-9-one (I) (89·5%), m.p. 113·4—114·6°. With Et_2O–MgMeBr (excess) this gives 2 : 9 : 10-trimethylanthracene (II) (28%), m.p. 95·6—96·5° (101—101·4°) (lit. 100—101°, 95—96°), and 2-methylanthraquinone (III) (27%). A red compound, 1(II) + 2(III), is characteristic of *meso*alkyl compounds. CrO_3 oxidises (II) to (III). 10-Acetoxyanthr-9-one, m.p. 108·8—110·8°, with MgMeBr–Et_2O gives a complex, decomposed by acid to 9 : 10-dimethylanthracene (IV) (58%), m.p. 183—184·4°, and anthraquinone (V) (40·5%), but by aq. NH_4Cl to 9 : 10-*dimethyl*-9 : 10-*dihydroanthranol* (18·5%), decomp. ~125° [with a trace of acid gives (IV)], and anthraquinol (38%). 9 : 10-Diphenylanthracene (12%), m.p. 250—252° (lit. 241—243°), and (V) (67%) are similarly obtained by use of MgPhBr. Replacement of OAc by Me or Ph is due to the "acidic" surroundings of $C_{(9)}$, since $CPh_3{\cdot}OAc$ (but not other analogous compounds) with MgMeBr gives CPh_3Me (69%). 10-*Benzoyloxyanthr*-9-*one* (prep. from the 10-Br-compound by AgOBz–C_6H_6; 41·5% yield), m.p. 130·6—131·8°; with 7 mols. of MgMeCl in Et_2O–C_6H_6 gives (IV) (50%), (V) (25%), BzOH (11%), and a little $CPhMe_2{\cdot}OH$, with 2·75 mols. (of MgMeBr) gives (V) (60%), (IV) (9%), BzOH (13%), and anthraquinol benzoate (7·5%), and with 2 mols. gives BzOH (41%), (V) (31%), and (IV) (25%). *o*-$C_6H_4Me{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$-*o* (VI) (prep. improved; 74% yield), forms, m.p. 110—115° and (stable) 129·6—132·6°, is reduced, after neutralisation, by H_2–Cu chromite in H_2O at 225°/2600 lb. to o-o'-*methylbenzylbenzoic acid* (93·5%), m.p. 128—131°, which in HF gives 4-*methylanthr*-9-*one* (VII) (77%), *forms*, m.p. (stable) 128—129·5° and 125·5—129·5° (*acetate*, m.p. 92—95·5°) [stated by von Braun *et al.* (A., 1926, 729) to be 1-methylanthr-9-one, m.p. 126—127°]. 1-Methylanthraquinone [prep. from (VI) by conc. H_2SO_4 at 100°; 97% yield), m.p. 171—173·4°, with H_2–Cu chromite in EtOH at (finally) 170°/1800 lb. gives 49·5% of (VII) (m.p. 127—129·5°). *m*-4-Xylidine (Ac derivative, m.p. 127—129°) gives 1 : 3 : 5 : 4-$C_6H_2Me_2Br{\cdot}NH_2$, which by diazotisation and treatment with Na_2SnO_2 gives 73% of 1 : 3 : 5-$C_6H_3Me_2Br$,

b.p. 88—89°/12 mm. The derived Mg compound with *o*-$C_6H_4(CO)_2O$ in Et_2O–C_6H_6 gives o-3′ : 5′-*dimethylbenzoylbenzoic acid* (47·5%), m.p. 178·2—180·2°, and $+H_2O$ (lost at 148°), m.p. 178°, hydrogenated at 200° to o-3′ : 5′-*dimethylbenzylbenzoic acid* (50%), m.p. 148·2—150·2°. In HF this gives 1 : 3-dimethylanthr-9-one (**VIII**) (93%), converted by bromination and then interaction with AgOAc–AcOH into 10-*acetoxy*-1 : 3-*dimethylanthr*-9-*one*, m.p. 107—108·5°, which with MgMeBr in boiling Et_2O gives 1 : 3-dimethyl-anthraquinone (**IX**) (32%) and -anthracene (a little) and 1 : 3 : 9 : 10-*tetramethylanthracene* (**X**) (a little), m.p. 85—87° (*picrate*, m.p. 136·5—138°), or at room temp. less (**IX**), more (**X**), and some (**VIII**). 9-Fluorenyl acetate and *O*-acetylmandelic acid with MgMeI give only fluorenol (89·5%) and mandelic acid (80·5%), respectively. O-*Mesitoylmandelic acid*, m.p. 166—169·8°, gives 19% of mesitoic acid and an oil in an incomplete reaction. M.p. are corr.

R. S. C.

Formation and structure of organic molecular compounds. J. Weiss (*J.C.S.*, 1942, 245—252; cf. A., 1941, II, 190).—Formation of the deeply coloured mol. compounds from quinones or NO_2-compounds and certain unsaturated hydrocarbons and their derivatives is ascribed to a complex mol., essentially ionic in character, formed by an electron transfer from the unsaturated hydrocarbon (donor A) to the quinone or NO_2-compound (acceptor B) according to the reaction $A + B \rightleftharpoons [A]^+[B]^-$. A quantum-mechanical discussion of the process is given, and points raised in support of the theory include: structure and rate of formation of mol. compounds; heats of formation; equilibrium in solution; colour of mol. compounds; crystal structure and intermol. distances; dipole moment and electrical conductivity in solution; relationship to semiquinones and other free radicals and radical ions. A. T. P.

2-Methyl-1 : 4-naphthaquinone derivatives. J. S. Buck and A. E. Ardis (*J. Amer. Chem. Soc.*, 1942, **64**, 725—726).—2-*Methyl*-1 : 4-*naphthaquinol H succinate acetate*, m.p. 129°, 2-*methyl*-1 : 4-*naphthaquinone*-p-*carboxyphenyl*-, m.p. 265° (decomp.), -*guanyl*-, m.p. 218° (decomp.), and *pyridinium chloride acet*-, m.p. 241° (decomp.), -*hydrazone* are prepared. The first is unstable, the others are ineffective (chicks) in 12-μg. doses. R. S. C.

Relation between absorption spectra and constitution of acid anthraquinone dyes. C. F. H. Allen, C. V. Wilson, and G. F. Frame (*J. Org. Chem.*, 1942, **7**, 169—182).—The absorption spectra of a no. of acid anthraquinone dyes have been recorded and the effect of certain atoms or groups in various positions in the mol. is discussed. The absorption curves of these dyes fall into two general groups, one having a smooth curve whereas the other is characterised by a double head. It appears that when there are in the 1- and 4-positions two groups which can furnish electrons by a mesomeric shift, the main band of the curve has a double head. If only one group of this type is present, there is only a single head. The twofold shift of electrons originating, *e.g.*, with unshared pairs of electrons of N or O atoms appears to be responsible for the differentiation of the one head into two. If the unshared pair of electrons on N is restrained from a shift towards the anthraquinone nucleus, the type of curve with a single head will probably result. Such restraint can be effected by SO_3H in the C_6H_6 ring attached to N (as in 1 : 4- and 1 : 5-diarylaminoanthraquinones). Sulphonation in the 3′ or 4′ position has this effect; the restraint is attributed to the strong conductive effect of the positive S atom which is transmitted through the aromatic ring system to the N atom and its unshared pair of electrons. When SO_3H is in the 2′ position a H bond is developed by the sharing of an electron pair of an O atom with the H of NH. H, in turn, to some extent releases electrons shared with the N atom so that the effect of SO_3H on the rest of the mol. is diminished.

H. W.

IV.—STEROLS AND STEROID SAPOGENINS.

Insect nutrition: nature of the fat-soluble factor.—See A., 1942, III, 538.

Steryl sulphates. II. Isolation and separation of sterols. IV. Thermal decomposition of calcium cholesteryl sulphate. A. E. Sobel and P. E. Spoerri (*J. Amer. Chem. Soc.*, 1942, **64**, 361—363, 482—483; cf. A., 1941, II, 250).—II. Sterols are readily isolated by conversion, usually by C_5H_5N,SO_3 in C_6H_6 at 56—60°, into C_5H_5N sulphates (and sometimes thence by KCl into the K sulphates), which in dil. acid regenerate the sterols. Separation of cholesterol from the thermal decomp. products of its Ca or K sulphate and from its acetate and isolation of ergosterol from yeast are described.

IV. Ca cholesteryl sulphate at 100° (dry) gives *dicholesteryl ether*, m.p. 192—194°, in boiling H_2O gives very slowly cholesterol (**I**), and in boiling C_6H_6 gives $CaSO_4$, H_2SO_4, and a S-free compound [not (**I**)], but is unchanged in boiling Et_2O or Pr^{β}_2O. R. S. C.

Location of the ethylenic linking in clionasterol. W. Bergmann and C. A. Kind (*J. Amer. Chem. Soc.*, 1942, **64**, 473—474).—Clionasterol is a Δ^5-sterol and is thus not identical with the sterol from *Spongilla lacustris* (A., 1941, II, 289). With $Al(OPr^{\beta})_3$ it gives Δ^4-*clionastenone* (**I**), m.p. 79° (3 : 5-*dinitrophenylhydrazone*, m.p. 230°; absorption spectrum of a $\Delta^{\alpha\beta}$-ketone), with H_2O_2 gives *clionastane*-3 : 5 : 6-*triol*, m.p. 238°, and with SeO_2 gives Δ^4-*cliostene*-[?-*clionastene*-]3 : 6-*diol*, m.p. 232° [gives (**I**) when dehydrated].

R. S. C.

Autoxidation of sterols in colloidal aqueous solution. II. Δ^6-Cholestene-3(β) : 5-diol, a rearrangement product of 7(β)-hydroxycholesterol. S. Bergström and O. Wintersteiner (*J. Biol. Chem.*, 1942, **143**, 503—507; cf. A., 1942, II, 102).—The cholestenediol, m.p. 137—138°, isolated from the products formed by autoxidation of cholesterol in colloidal solution is a Δ^6-*cholestene*-3(β) : 5-*diol* (**I**), formed by allylic rearrangement of probably 7(β)-hydroxycholesterol. Hydrogenation (PtO_2; AcOH) of (**I**) yields a mixture (pptd. by digitonin) of β-cholestanol (**II**) and β-coprostanol; this with Na in boiling xylene affords (**II**) and α-coprostanol. (**I**) is oxidised by $Al(OPh)_3$–C_6H_6–$COMe_2$ to $\Delta^{4:6}$-cholestadien-3-one, m.p. 80—81°. M.p. are corr. A. T. P.

Steryl sulphates. III. Preparation of cholestane-3 : 5 : 6-triol-*I*. A. E. Sobel, I. A. Kaye, and P. E. Spoerri (*J. Amer. Chem. Soc.*, 1942, **64**, 471—472).—C_5H_5N 5 : 6-dibromocholestanyl sulphate with 0·5M-K_2CO_3 at room temp. and then boiling H_2SO_4–aq. EtOH on the product formed gives cholestane-3 : 5 : 6-triol-*I*, m.p. 234° (3 : 6-diacetate, m.p. 166°). R. S. C.

Sterols. CXXXIII. Sapogenins. LV. 20-Methylpregnanetriol and related compounds. R. E. Marker and D. L. Turner (*J. Amer. Chem. Soc.*, 1942, **64**, 481—482).—Tigone diacetate (prep. by oxidation of ψ-tigogenin diacetate) with MgMeI–Et_2O gives 20-*methyl*allo*pregnane*-3(β) : 16 : 20-*triol* (**I**), m.p. 262—264°. With MgMeI the oxidation product from ψ-sarsasapogenin diacetate gives 20-*methylpregnane*-3(β) : 16 : 20-*triol*, m.p. 234—236°, and diosone diacetate (the product from ψ-diosgenin) gives 20-*methyl*-Δ^5-*pregnene*-3(β) : 16 : 20-*triol*, m.p. 275—276°, reduced by H_2–PtO_2 in MeOH at 3 atm. to (**I**) and oxidised by $Al(OBu^{\gamma})_3$–C_6H_6–$COMe_2$ to 20-*methyl*-$\Delta^{17:20}$-*pregnene*-3 : 16-*dione*, m.p. 193—195°. R. S. C.

Synthesis of an isomeride of œstrone containing a phenolic ring B. W. E. Bachmann and A. B. Ness (*J. Amer. Chem. Soc.*, 1942, **64**, 536—540).—5 : 6 : 7 : 8-Tetrahydro-α-naphthol (prep. from α-$C_{10}H_7$·OH by Na in fusel oil in 87% yield or by H_2–Raney Ni at 150°/150 atm.) with Me_2SO_4–aq. NaOH gives the Me ether (88%), which with $(CH_2{\cdot}CO)_2O$–$AlCl_3$–$PhNO_2$ at 0—5° gives γ-*keto*-γ-4-*methoxy*-5 : 6 : 7 : 8-*tetrahydro*-1-*naphthyl*-n-*butyric acid* (82%), m.p. 176—177°. Zn–Hg in HCl–AcOH–H_2O–PhMe then yields γ-4-*methoxy*-5 : 6 : 7 : 8-*tetrahydro*-1-*naphthyl*-n-*butyric acid* (**I**) (75%), m.p. 122—123°, the Me ester (CH_2N_2) of which with Pd–C at 250—280° gives the known γ-4-methoxy-1-naphthyl-*n*-butyric acid (proof of structure). Addition of PCl_5 at 10° and then of $SnCl_4$ to the cooled solution of (**I**) in C_6H_6 gives 1-*keto*-9-*methoxy*-s-*octahydrophenanthrene* (**II**) (80—90%), m.p. 89·5—90°, the semicarbazone, m.p. 269—271°, of which with NaOEt–EtOH at 180° gives 9-*methoxy*-s-*octahydrophenanthrene*, m.p. 90—91°, and thence (Pd–C; 245—250°, later 285—300°) 9-methoxyphenanthrene (50%). With NaOEt–$Me_2C_2O_4$–C_6H_6–N_2, (**II**) yields *Me* 1-*keto*-9-*methoxy*-s-*octahydrophenanthrene*-2-*glyoxylate* (92%), m.p. 125—126·5°, which with soft glass powder at 180° gives the *Me* 2-*carboxylate* (88—97%), m.p. 103—103·5°. The Na enolate thereof with MeI–N_2 gives *Me* 1-*keto*-9-*methoxy*-2-*methyl*-s-*octahydrophenanthrene*-2-*carboxylate* (**III**) (93%), m.p. 138·5—139°, and thence (Reformatsky) *Me* 1-*hydroxy*-2-*carbomethoxy*-9-*methoxy*-2-*methyl*-s-*octahydrophenanthrene*-1-*acetate* (**IV**) (90—95%), m.p. 145—146·5°. Dehydration of (**IV**) by $SOCl_2$–C_5H_5N–C_6H_6 and subsequent treatment with boiling KOH–MeOH gives mixed K_2 salts (*A*); the acids at 60—70° give anti-2-*carboxy*-9-*methoxy*-2-*methyl*-s-*octahydrophenanthrylidene*-1-*acetic acid* (**V**), m.p. 208·5—209°, and the *anhydride*, m.p. 227·5—228·5°, of the *syn*-form. Alkaline hydrolysis of the Me_2 ester, m.p. 85—86°, of (**V**) gives the *H ester*, m.p. 103—104°, oxidised ($KMnO_4$) to (**III**), which proves absence of migration. Reduction of *A* by 2% Na–Hg gives 2-*carboxy*-9-*methoxy*-2-*methyl*-s-*octahydrophenanthrene*-1-*acetic acid*, α-, m.p. 219—220°, and β-*form*, m.p. 233·5—234° (decomp.), and thence by known methods *Me*$_2$, α-, m.p. 115·6—116°, and β-*form*, 70—71° (clear at 93—94°), and 2-*Me* 1-*H* ester, α-, m.p. 174·5—176°, and β-*form*, m.p. 118—120°, *Me* β-2-*carbomethoxy*-9-*methoxy*-2-*methyl*-s-*octahydro*-1-*phenanthrylpropionate*, α-, m.p. 94—94·5°, and β-*form*, m.p. 115·5—116°, *Me* 6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-17-*equilenone*-16-*carboxylate*, α-, m.p. 146—147° (decomp.; vac.), and β-*form*, m.p. 129·5—130° (vac.), and 6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-17-*equilenone*, α- (**VI**), m.p. 118—118·5° (vac.), and β-*form* (**VII**), m.p. 108—109°. In boiling 48% aq. HBr + AcOH–N_2, (**VI**) gives 6-*hydroxy*-1 : 2 : 3 : 4-*tetrahydro*-17-*equilenone* (**VIII**), m.p. 150—150·5°, but (**VII**) gives a substance, m.p. 203·5—204° (vac.). (**VIII**) has no œstrogenic activity in 1-mg. doses. R. S. C.

Sterols. CXXVII. 17-Bromopregnan-3(β)-ol-20-one. CXXVIII. 17 : 21-Dibromopregnan-3(β)-ol-20-one. Its conversion into pregnane-3(β) : 21-diol-20-one. R. E. Marker, H. M. Crooks, jun., and R. B. Wagner. **CXXIX. Rearrangement of 17-bromopregnan-3(β)-ol-20-one.** R. E. Marker and R. B. Wagner (*J. Amer. Chem. Soc.*, 1942, **64**, 210—213, 213—215, 216—218).—CXXVII. With Br and a trace of HBr in AcOH pregnan-3(β)-ol-20-one (**I**) at 25° or its acetate (**II**) at 30° gives 60—70% of 17-*bromopregnan*-3(β)-*ol*-20-*one*

(**III**), m.p. 169—171°, or its *acetate* (**IV**), m.p. 152—154°, respectively. (**III**) is reduced by Zn dust in AcOH at 100° or H_2–Pd–$BaSO_4$–C_5H_5N in MeOH to (**I**); (**IV**) is debrominated similarly or by Fe powder in AcOH at 100° to (**II**). Boiling C_5H_5N converts (**I**) and (**II**) into Δ^{16}-pregnen-3(β)-ol-20-one (**V**) and its acetate (**VI**), respectively. CrO_3–AcOH oxidises (**III**) to a non-cryst. product which is converted by boiling C_5H_5N or H_2–Pd–$BaSO_4$–C_5H_5N–MeOH into Δ^{16}-pregnene- (**VII**) or pregnane-3 : 20-dione [obtained also from (**VII**) by Zn dust in AcOH at 100°], respectively.

CXXVIII. With 2 mols. of Br and a little HBr in AcOH at 40°, (**I**) and (**II**) give 17 : 21-*dibromopregnan*-3(β)-*ol*-20-*one* (**VIII**), m.p. 190—192°, and its *acetate* (**IX**), m.p. 190—191°, respectively. With Fe powder in AcOH at 100°, (**VIII**) gives (**I**), and (**IX**) gives (**II**) similarly or with Zn dust in AcOH at 100°. With KOAc in boiling AcOH, (**VIII**) and (**IX**) give 21-*bromo*-Δ^{16}-*pregnen*-3(β)-*ol*-20-*one* (**X**), m.p. 155—157°, and its *acetate* (**XI**), m.p. 151—154°, respectively. Reduction of (**XI**) by Zn dust in AcOH at 100° or H_2–Pd–C_5H_5N–MeOH and later hydrolysis by boiling $KHCO_3$–MeOH gives (**I**), but H_2–Pd–$BaSO_4$ in dioxan (no C_5H_5N) at 3 atm. reduces (**X**) or (**XI**) to 21-*bromopregnan*-3(β)-*ol*-20-*one* (**XII**), m.p. 127—128°, or its *acetate* (**XIII**), m.p. 145—147°, respectively. With KOAc in boiling AcOH, (**XII**) and (**XIII**) give 21-*acetoxypregnan*-3(β)-*ol*-20-*one*, m.p. 121—123° [and, by an allylic rearrangement, some (**V**)], and 3(β) : 21-*diacetoxypregnan*-20-*one*, m.p. 145—146° [and some (**VI**)], respectively.

CXXIX. The Aston–Greenburg rearrangement (A., 1941, II, 4) occurs in the (*tert.*) 17-bromopregnane series. With $KHCO_3$ in boiling MeOH–H_2O, (**XIII**) gives *Me* 3(β)-*hydroxy*-17-*methylætiocholanate* (**XIV**), *forms*, m.p. 143—145° and 124—126° [*acetate* (**XV**) (prep. by Ac_2O), m.p. 136°, which is unaffected by $POCl_3$–C_5H_5N at 135°, H_2–PtO_2 in MeOH–Et_2O at 3 atm., or CrO_3–AcOH at 55°, and gives no semicarbazone]. Heating (**XV**) in 1 : 1 : 5 KOH–H_2O–EtOH for 4 days gives 3(β)-*hydroxy*-17-*methylætiocholanic acid*, m.p. 222—224° (*acetate*, m.p. 220—222°, prepared by Ac_2O–C_5H_5N at room temp.), which with CrO_3–AcOH at room temp. gives 3-*keto*-17-*methylætiocholanic acid* (**XVI**), m.p. 224—226°. Na–EtOH reduces (**XV**) to 17-*methyl*-21-*norpregnane*-3(β) : 21-*diol*, m.p. 124° (isolated as *diacetate*, m.p. 94—95°), which with CrO_3–AcOH at room temp. gives (**XVI**) or by more prolonged treatment a *tricarboxylic acid*, $C_{21}H_{32}O_6$, m.p. 279° (decomp.), formed by fission at $C_{(3)}$. CrO_3–AcOH oxidises (**XIV**) to *Me* 3-*keto*-17-*methylætiocholanate*, m.p. 103—105°, which is reduced by H_2–PtO_2 in dioxan at 3 atm. to *Me* 3(α)-*hydroxy*-17-*methylætiocholanate*, m.p. 152—153° (isolated as *acetate*, m.p. 130—131°; no digitonide), or by Na–EtOH to 17-methylnorpregnane-3(α) : 21-diol, isolated as *diacetate*, m.p. 123—125°, resolidifies, remelts at 156°. R. S. C.

Sterols. CXXX. 3 : 6-Diketo-sterols and their reduction products. R. E. Marker, H. M. Crooks, jun., E. M. Jones, and E. L. Wittbecker (*J. Amer. Chem. Soc.*, 1942, **64**, 219—220).—Treatment of sitosterol at 15—20° or stigmasterol at 20—22° with CrO_3–AcOH and then with Zn dust in boiling AcOH containing a little H_2O gives *sitostane*- (**I**), m.p. 196—199°, and *stigmastene*-3 : 6-*dione* (**II**), m.p. 194—196°, respectively. H_2–PtO_2 in AcOH at 45 lb. reduces (**I**) or (**II**) to *sitostane*-3(β) : 6(β)-*diol*, m.p. 204—206°, the *diacetate*, m.p. 111—113°, of which with CrO_3 in AcOH–H_2O (80 : 18) at 90—95° gives nor*allo*hyodeoxycholic acid. Similar treatment of 3-hydroxy-Δ^5-cholenic acid with CrO_3 and then Zn dust in AcOH gives dehydro-*allo*- and thence (H_2–PtO_2–AcOH) *allo*-hyodeoxycholic acid. 3-Hydroxy-Δ^5-bisnorcholenic acid gives *dehydrobisnor*allo-, m.p. 244—247°, and *bisnor*allo-*hyodeoxycholic acid*, m.p. 258—260°, also obtained by Wieland degradation of *allo*hyodeoxycholic acid. *allo*-Pregnane-3 : 6 : 20-trione and H_2–PtO_2 in AcOH at 3 atm. give allo*pregnane*-3(β) : 6(β) : 20(β)-*triol*, m.p. 222—224° (*triacetate*, m.p. 163—165°). R. S. C.

Acids of the *cyclo*pentanophenanthrene series.—See B., 1942, III, 157.

Steroids and sex hormones. LXXIV. Preparation of 14-deoxydigitoxigenin [3(α) : 21-dihydroxy-$\Delta^{20:22}$-norcholenolactone]. L. Ruzicka, P. A. Plattner, and G. Balla (*Helv. Chim. Acta*, 1942, **25**, 65—78).—Cholestenone (**I**) in presence of 5% of its wt. of Raney Ni in EtOH is hydrogenated very slowly and after absorption of 2 H leads to a mixture of cholestanol with much unchanged (**I**); if hydrogenation is continued to the limit, a difficultly separable mixture and ~45% of *epi*coprostanol result. With equal wts. of (**I**) and catalyst in presence of NaOH or NaOEt hydrogenation is very rapid and the crude product, which contains considerable material pptd. by digitonin, can be worked directly to yield *epi*coprosterol. Δ^4-3-Ketoætiocholenic acid is only slowly hydrogenated in EtOH even in presence of much catalyst, giving ~40% yield of 3(β)-hydroxyætiocholanic acid, isolated as the Me ester, m.p. 129—131°. In presence of alkali the action is much more rapid, giving ~30% of 3(β)-hydroxy*allo*ætiocholanic acid (Me ester, m.p. 165—170°) with considerable amounts of nearly inseparable mixtures. Better results are obtained by hydrogenating Me Δ^4-3-ketoætiocholenate, which can be conducted almost homogeneously as far as the configuration of the rings A/B is concerned. The crude product is best treated with BzCl in C_5H_5N, after which *Me* 3(β)-*benzoyloxy*allo*ætiocholanate*, m.p. 210—212°, $[\alpha]_D$ +38° in $CHCl_3$ [hydrolysed to 3(β)-*hydroxy*-allo*ætiocholanic acid* (also +0·5EtOH), m.p. 247—249°], is removed through its sparing solubility in light petroleum. The sol. products are separated chromatographically into *Me* 3(α)-*benzoyloxyætiocholanate*, m.p. 105—107°, $[\alpha]_D$ +78° in $CHCl_3$ [whence the α-OH-acid (**II**), m.p. 274—276°, $[\alpha]_D$ +49·6° in dioxan], and *Me* 3(β)-*benzoyloxyætiocholanate*, m.p. 155—157°, $[\alpha]_D$ +50·4° in $CHCl_3$ (whence the β-*OH*-acid, m.p. 226—228°, $[\alpha]_D$ +36·8° in $CHCl_3$). (**II**) is converted into its Ac derivative, m.p. 230—232°, $[\alpha]_D$ +81° in $CHCl_3$, which by successive treatments with $SOCl_2$ in C_6H_6 and CH_2N_2 gives 21-*diazo*-3(α)-*acetoxypregnan*-20-*one*, m.p. 140—142° (decomp.), $[\alpha]_D$ +189° in $CHCl_3$; in hot AcOH this passes into 3(α) : 21-*diacetoxypregnan*-20-*one*, m.p. 60—70° and, after resolidification, m.p. 86—88°, $[\alpha]_D$ +106° in $CHCl_3$, which with Zn and $CH_2Br{\cdot}CO_2Et$ gives the unsaturated *lactone acetate*, $C_{25}H_{36}O_4$, m.p. 166—167°, $[\alpha]_D$ +42° in $CHCl_3$ (strong, positive Legal test), and 20 : 21-*dihydroxy*-3(α)-*acetoxynorcholanolactone* (**III**), m.p. 204—207° (decomp.), $[\alpha]_D$ +58° in $CHCl_3$. (**III**) is hydrolysed to 14-*deoxydigitoxigenin* [3(α) : 21-*dihydroxy*-$\Delta^{20:22}$-*norcholenolactone*], m.p. 225—227°. M.p. are corr. (vac.). H. W.

Steroids and sex-hormones. LXXV. Preparation of 3(β) : 21-dihydroxy-$\Delta^{20:22}$-nor*allo*cholenolactone. L. Ruzicka, P. A. Plattner, and A. Fürst (*Helv. Chim. Acta*, 1942, **25**, 79—84).—The absorption max. of strophanthidin (**I**), digoxigenin diacetate, and 21-hydroxy-3(β)-acetoxy-$\Delta^{20:22}$-nor*allo*cholenolactone are practically identical and the curves of 14-deoxydigitoxigenin, (**I**), and 21-hydroxy-3(β)-acetoxy-$\Delta^{5:6,20:22}$-norcholadienolactone (**II**) are coincident. (**II**) is obtained by the action of Zn filings and $CH_2Br{\cdot}CO_2Et$ on pregnenonediol diacetate and treatment of the product with boiling Ac_2O. 20 : 21-Dihydroxy-3(β)-acetoxy-Δ^5-norcholenolactone (**III**), m.p. 248—252° (decomp.), $[\alpha]_D$ −22° in $CHCl_3$, is dehydrated by boiling Ac_2O–C_5H_5N to (**II**). Hydrogenation (PtO_2 in AcOH) of (**III**) leads to 20 : 21-*dihydroxy*-3(β)-*acetoxynor*allo*cholanolactone*, m.p. 260—263° (decomp.), $[\alpha]_D$ +35·7° in dioxan, +32·3° in $CHCl_3$, transformed by protracted boiling with Ac_2O into 21-*hydroxy*-3(β)-*acetoxy*-$\Delta^{20:22}$-*nor*allo*cholenolactone* (**IV**), m.p. 193—194°, $[\alpha]_D$ −1·06° in $CHCl_3$. The residues from (**IV**) are converted by 2N-HCl in dioxan into 3(β) : 21-*dihydroxy*-$\Delta^{20:22}$-*nor*allo*cholenolactone*, m.p. 248—250°. M.p. are corr. (vac.). H. W.

Sterols. CXXXII. Sapogenins. LIV. Action of hydrogen peroxide on ψ-sapogenin acetates and pregnenolones. R. E. Marker, E. M. Jones, and E. L. Wittbecker (*J. Amer. Chem. Soc.*, 1942, **64**, 468—469).—ψ-Sarsasapogenin diacetate with 30% H_2O_2 in AcOH at 70° and then boiling KOH–MeOH gives Δ^{16}-pregnen-3(β)-ol-20-one, the acetate of which on further oxidation gives the *acetate*, m.p. 179—180°, of a *substance*, $C_{21}H_{32}O_3$, m.p. 223—225°. ψ-Tigogenin diacetate gives similarly Δ^{16}-*allo*pregnen-3(β)-ol-20-one acetate and thence a *substance*, $C_{21}H_{32}O_3$, m.p. 181—182° (*acetate*, m.p. 185—186°). R. S. C.

Sterols. CXXXI. Sapogenins. LIII. Configuration of the hydroxyl groups in chlorogenin. R. E. Marker, D. L. Turner, and E. L. Wittbecker (*J. Amer. Chem. Soc.*, 1942, **64**, 221—223).—The β-configuration of the OH at $C_{(3)}$ of chlorogenin (**I**) is proved. Steroid sapogenins behave normally with digitonin; Noller's "solubility product" (A., 1939, II, 546) has no meaning. Chlorogenone and $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ give β-chlorogenin and (**I**) (both giving digitonides) with epi*chlorogenin* (**II**), m.p. 270—274°. Na–$C_5H_{11}{\cdot}OH$ converts (**II**) into (**I**), on which it has no effect. With Na–$C_5H_{11}{\cdot}OH$ *epi*-tigogenin yields tigogenin. With CrO_3–AcOH and later a little Zn dust in AcOH, (**I**) gives chlorogenone (no digitonide) and ketonic digitonide-forming material, which with Zn–EtOH–conc. HCl gives tigogenin. R. S. C.

Sterols. CXXXIV. Structure of ouabain. R. E. Marker, D. L. Turner, T. S. Oakwood, E. Rohrmann, and P. R. Ulshafer (*J. Amer. Chem. Soc.*, 1942, **64**, 720—721).—Ring A and not B (cf. Fieser *et al.*, A., 1936, 1116) of hepta-acetyldeoxydihydro-ouabain becomes aromatic on acetolysis. Neoergosterol (**I**) with H_2–PtO_2 in AcOH, Et_2O, or HCl–EtOH and later boiling 3% KOH–EtOH gives 22 : 23-*dihydroneoergosterol*, m.p. 146—148° [*acetate*, m.p. 120·5—121·5°, also obtained by hydrogenation of the acetate (**II**) of (**I**)], oxidised by CrO_3–AcOH to acidic products. Dehydroneoergosterol with H_2–PtO_2 in HCl–EtOH or AcOH gives a hydrocarbon, $C_{27}H_{42}$, m.p. 64—65°, also obtainable from (**II**). With $Al(OPr^{\beta})_3$–*cyclo*hexanone–PhMe, (**I**) gives a *ketone*, $C_{27}H_{38}O$, m.p. 121—122·5° (*semicarbazone*, m.p. >295°), also obtained by distilling *epi*neoergosterol with Cu powder. R. S. C.

Sterols. CXXXV. Sapogenins. LVI. Sarsasapogenoic acid. R. E. Marker and A. C. Shabica (*J. Amer. Chem. Soc.*, 1942, **64**, 721—722).—Me sarsasapogenoate (**I**) (prep. by CH_2N_2), m.p. 132—134°, with NH_2OH,HCl–KOAc–MeOH at 130° gives a *dioxime*, m.p. 169—171°, without loss of C (cf. Fieser *et al.*, A., 1939, II, 31). The acid obtained by oxidation of dihydrosarsasapogenin acetate (A., 1939, II, 276) is shown (mixed m.p. of the acid and ester) to be identical with anhydrotetrahydrosarsasapogenoic acid (Fieser, *loc. cit.*); this is confirmed by reduction of (**I**) by Na–EtOH to dihydrosarsasapogenin. R. S. C.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Synthetic production of camphor from pinene. III. Borneol, *iso*borneol, and their esters. B. G. S. Acharya, R. C. Shah, and T. S. Wheeler (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 106—117).—Pinene (**I**) and its hydrochloride (**II**) are not suitable for the direct production of borneols and thence camphor (**III**). Camphene appears to be a necessary step in the process. The max. yield of borneol (**IV**) by the action of (**I**) on AcOH, HCO_2H, $EtCO_2H$, Pr^nCO_2H, stearic, palmitic, or oleic acid, *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ (**V**), $H_2C_2O_4$, *o*-$C_6H_4(CO_2H)_2$, or *o*-$C_6Cl_4(CO_2H)_2$ is obtained with (**V**), the best results being obtained with 1·75 mols. of (**V**) at 100—110° for 60 hr.; the yield of ester is not increased by using condensing agents (H_2SO_4, $ZnCl_2$, NaOAc), catalysts, solvents, or diluents and compounds of the acid such as the Me, Et, and Pr esters. Benzoic, picric, citric, and tartaric acid, H_2SO_4, and PhOH are unsatisfactory. (**I**) and glacial AcOH are condensed at ordinary and increased pressure with and without condensing agents and catalysts; the max. yield of ester obtained is 58% but this in all cases is a mixture which gives little (**III**) when hydrolysed. Equimol. amounts of (**I**) and anhyd. $H_2C_2O_4$ in boiling CCl_4 (2 vols.) containing 2% of $FeCl_3$ as catalyst for 4—6 hr. gives 18% of (**IV**), which, however, gives only a 40% yield of (**III**). $CCl_3{\cdot}CO_2H$ gives a 17% yield of crude (**IV**) which gives little (**III**) when oxidised. The esters are best hydrolysed with solid NaOH. Details are given of the action on (**II**) of the acids listed above. The max. yield of *iso*borneol (18%) is obtained with AcOH; in most cases the "borneols" are crude and give poor yields of (**III**) on oxidation. Much better results are recorded for the "esterification" of camphene with these acids. AcOH is the cheapest and most suitable, good results being obtained with the hydrocarbon and acids (1 : 2·5) at 45—55° for 2·5 hr. in the presence of 50% H_2SO_4. H. W.

Kinetics of the mutarotation of aminomethylene-*d*-camphor.—See A., 1942, **I**, 242.

Structure of cadinene. W. P. Campbell and M. D. Soffer (*J. Amer. Chem. Soc.*, 1942, **64**, 417—425).—Cadinene (**I**) is shown to be 1 : 6-*dimethyl*-4-iso*propyl*-$\Delta^{1:6}$-*hexahydronaphthalene*. Its reaction with Bz_2O_2 is faster in $CHCl_3$ than in Et_2O or EtOAc. Its nearly pure dioxide with MgMeCl in boiling Et_2O gives an oil, converted by Se at 135° and later 180—190° (N_2) into, *inter alia*, 1 : 2 : 6 : 7-*tetramethyl*-4-iso*propylnaphthalene* (**II**), m.p. 102—103° (*picrate*, m.p. 145°). The mono-oxide gives similarly (Se finally at 310—330°) (**I**), 1 : 2 : 6 : 4-$C_{10}H_4Me_3Pr^{\beta}$ (**III**) [*picrate*, m.p. 143·5—144°; *styphnate*, m.p. 170·5—171°; $C_6H_3(NO_2)_3$ *compound*, m.p. 170·5—171°], and 1 : 6-$C_{10}H_6Me_2$. With CrO_3–AcOH at 65°, later 45—50° and 60°, (**II**) gives an oil, oxidised by HNO_3–H_2O to 1 : 2 : 4 : 5-$C_6H_2(CO_2H)_4$ (**IV**). 3 : 4 : 1-$C_6H_3Me_2{\cdot}CO{\cdot}[CH_2]_3{\cdot}CO_2Me$ (prep. from the acid by MeOH–H_2SO_4), b.p. 161—162°/1·5 mm. (semicarbazone, m.p. 157—157·5°), with MgMeI in Et_2O at, successively, −5°, room temp., and the b.p. gives mixed *γ*-4-*o*-xylyl-*n*-Δ^{β}-pentenoic acids (62%) (a *form*, m.p. 78—80°, is isolated), hydrogenated (PtO_2) in AcOH to *γ*-4-*o*-*xylyl*-n-*valeric acid* (86%), b.p. 146—147°/1 mm., which in HF at room temp. or 80% H_2SO_4 at 100° gives 1-*keto*-4 : 6 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 30° (28·5—30°). [*semicarbazone*, m.p. 238° (decomp.); oxidised by HNO_3–H_2O at 180° and later 190° to (**IV**)]. With $Me_2C_2O_4$–NaOMe–MeOH this gives *Me* 1-*keto*-4 : 6 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*glyoxylate*, *enol* form (85%), m.p. 77°, which with powdered glass at 180° gives the 2-*CO_2Me*-derivative (83%), b.p. 153—155°/1 mm., and thence (NaOMe–MeI) 1-*keto*-2-*carbomethoxy*-2 : 4 : 6 : 7-*tetramethyl*- (87%), b.p. 149—153°/0·9 mm. (form, m.p. 86—87°), and (hydrolysis and then decarboxylation) 1-*keto*-2 : 4 : 6 : 7-*tetramethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (89%) (form m.p. 89—89·5°). $MgPr^{\beta}Cl$–Et_2O at 0° and later the b.p. then gives a carbinol, which by dehydration (88% HCO_2H; 35—40°) and oxidation (chloranil in boiling xylene) gives 1 : 3 : 6 : 7-*tetramethyl*-4-iso*propylnaphthalene*, m.p. 96·5—97° (*picrate*, m.p. 156·5—157°). 1 : 2 : 4-$C_6H_3Me_2{\cdot}COMe$ (prep. from *o*-xylene by Ac_2O–$AlCl_3$ in CS_2; 90% yield), b.p. 123—126·5°/19 mm., gives successively (Reformatsky, then $KHSO_4$ at 155°, and finally aq. KOH) 3 : 4 : 1-$C_6H_3Me_2{\cdot}CMe{:}CMe{\cdot}CO_2H$ (28%), an oil, [H_2–PtO_2–AcOH) *β*-4-*o*-*xylyl*-*α*-*methyl*-n-*butyric acid* (92%), b.p. 156—161°/0·5 mm., (Arndt–Eistert) *γ*-4-*o*-*xylyl*-*β*-*methyl*-n-*valeric acid* (52%), b.p. 146—147°/0·2 mm., (80% H_2SO_4) 1-keto-3 : 4 : 6 : 7-tetramethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (71%), b.p. 137—139°/1·2 mm. [with HNO_3 gives (**IV**)], and ($MgPr^{\beta}Cl$ etc. as above) (**II**). 1-Keto-4 : 6 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene gives ($MgPr^{\beta}Cl$ etc.) 1 : 6 : 7-*trimethyl*-4-iso*propylnaphthalene*, m.p. 39·5—40° (*picrate*, m.p. 122—123°). *p*-$C_6H_4Me{\cdot}COMe$ gives, as above, *p*-$C_6H_4Me{\cdot}CMe{:}CMe{\cdot}CO_2H$, b.p. 155—157°/3·5 mm. (*form*, m.p. 133—133·5°), 1-keto-3 : 4 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 107—109°/0·4 mm., and (**I**). M.p. are corr. R. S. C.

Substances with the odour of violets. XII. Degradation of irone with ozone and chromic acid. L. Ruzicka, C. F. Seidel, H. Schinz, and M. Pfeiffer (*Helv. Chim. Acta*, 1942, **25**, 188—205).—Although the results of the degradation of irone (**I**) with O_3 and CrO_3 do not afford absolutely conclusive evidence of its constitution, in conjunction with previous transformations and with degradation and transformation experiments on di- and tetra-hydroirone they show that natural (**I**) consists mainly of the ketone $CH_2<^{CHMe{\cdot}CMe_2}_{CH_2{\cdot}CH{:}CH}>CH{\cdot}CH{:}CH{\cdot}COMe$. (**I**) is ozonised in AcOH and the product is further oxidised with CrO_3 (≡3·5—4 O). After removal of some very unstable neutral material from which nothing definite could be isolated, the acids are esterified (MeOH–H_2SO_4); the Me esters are purified by treatment with *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$,HCl and distilled. Thus are obtained Me_2 (+)-*ααβ-trimethylglutarate* (**II**), b.p. 104—106°/10 mm., Me_2 (+)-*ββγ-trimethylpimelate* (**III**), b.p. 104—106°/0·1 mm. and a (+)-Me_2 ester, $C_{12}H_{22}O_4$ (**IV**), b.p. 90—92°/0·1 mm. (**II**) is hydrolysed to the *dl*-acid, m.p. 113—114°, identified by comparison with the synthetic acid, its monoanilide, 155—156°, mono-*p*-toluidide, m.p. 162—163°, and mono-*β*-naphthylamide, m.p. 178—179°. (**III**) is hydrolysed to the *acid*, m.p. 58—60°, $[\alpha]_D$ +46° in C_6H_6, which passes at 310° into 3 : 3 : 4-*trimethyl*-cyclo*hexanone*, b.p. 126—128°/90 mm., $[\alpha]_D$ −23°, purified through the *semicarbazone*, m.p. 205—206°. This gives a *CHPh*: derivative, b.p. 142—144°/0·3 mm., ozonised to *ββγ-trimethylbutane-αδ-dicarboxylic acid*, m.p. 122—123°, $[\alpha]_D$ +7·4° in EtOH (*Me_2* ester, b.p. 127—131°/11 mm.), transformed at 310° into 3 : 3 : 4-*trimethyl*-cyclo*pentanone*, b.p. 86—87°/50 mm. (*semicarbazone*, m.p. 221—223°), the (*CHPh*:)$_2$ derivative, b.p. 195—200°/0·3 mm., of which is ozonised to *d*-trimethylsuccinic acid, m.p. 144—145° (*anil*, m.p. 156—157°; *β-naphthil*, m.p. 148—149°). (**IV**) is hydrolysed to an *acid*, $C_9H_{16}O_4$, m.p. 79—81°, which passes at 300—320° into a *trimethylcyclopentanone*, b.p. 94—96°/90 mm. (*semicarbazone*, m.p. 221—222°); its CHPh: derivative, b.p. 135—140°/0·5 mm., is ozonised to (+)-*αββ-trimethylglutaric acid*, m.p. 102—103°, $[\alpha]_D$ +9° in $CHCl_3$ (*Me_2* ester, b.p. 110—112°/15 mm.), which gives an ill-defined anhydride at 320°. Ag_2 *dl-αββ*-trimethylglutarate is transformed by the successive action of I and K_2CO_3 into the acid and the *lactone*, $C_7H_{12}O_2$, b.p. 88—89°/10 mm., which is oxidised to $CO_2H{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$. From the solids obtained by treatment of the ester fractions with *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$,HCl have been isolated the *p*-nitrophenylhydrazone of Me lævulate, m.p. 132—133°, and an *ester* p-*nitrophenylhydrazone*, $C_{18}H_{25}O_5N_3$, m.p. 120—121°, hydrolysed to the *acid*, (?) $C_{16}H_{21}O_5N_3$, m.p. 183—184°. The experiments described above were carried out with a sample of (**I**) purified through the non-cryst. compound with *p*-$NH_2{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3H$. Experiments are also described with two further samples obtained by hydrolysis of the phenylsemicarbazones, m.p. 177—179° and 155—160°, with *o*-$C_6H_4(CO)_2O$. The corresponding Me_2 ester fractions give only amorphous dicarboxylic acids which are decomposed at 300—310°; the m.p. of the semicarbazones obtained from these ketones show that (**I**) regenerated from cryst. derivatives gives only the dextrorotatory degradation acids and not $CO_2H{\cdot}CHMe{\cdot}CMe_2{\cdot}CO_2H$. H. W.

Optical activity of terpene compounds. Influence of solvent.—See A., 1942, I, 228.

VI.—HETEROCYCLIC.

Coumaran derivatives. IX. Synthesis of 2 : 3 : 5 : 3′ : 4′-pentahydroxy-1-benzylcoumaran. R. L. Shriner and F. Grosser (*J. Amer. Chem. Soc.*, 1942, **64**, 382—384; cf. A., 1941, II, 371).—2 : 4 : 6 : 1-$(OH)_3C_6H_2{\cdot}CO{\cdot}CH_2Cl$, m.p. 188—191° (decomp.), is obtained in 88% yield by condensing *s*-$C_6H_3(OH)_3$ and $CH_2Cl{\cdot}CN$ by $ZnCl_2$–HCl in Et_2O and hydrolysing the resulting ketimine hydrochloride by boiling H_2O. In, best (95% yield), boiling NaOAc–95% EtOH it gives 3 : 5-dihydroxy-1 : 2-dihydrobenzfuran-2-one (**I**), m.p. 255—260° (decomp.), which with 3 : 4 : 1-$(OH)_2C_6H_3{\cdot}CHO$ gives indefinite products. The *dibenzoate* (prep. by BzCl and K_2CO_3 in aq. $COMe_2$), m.p. 166—167°, of (**I**) with 3 : 4 : 1-$(OBz)_2C_6H_3{\cdot}CHO$ gives 92% of 3 : 5 : 3′ : 4′-*tetrabenzoyloxy*-1-*benzylidene*-1 : 2-*dihydrobenzfuran*-2-*one* (**II**), m.p. 188—192°. 3 : 5 : 3′ : 4′-*Tetrabenzoyloxy*-1-*benzyl*-1 : 2-*dihydrobenzfuran*-2-*ol*, prepared therefrom by H_2–PtO_2 in (*a*) dioxan or (*b*) AcOH at 25°/37 lb., has m.p. (*a*) 138—140° or (*b*) 135—137° (? diastereoisomerides) and in KOH–H_2O–EtOH–C_6H_6–N_2 gives 2 : 3 : 5 : 3′ : 4′-*pentahydroxy*-1-*benzyl*-1 : 2-*dihydrobenzfuran* (**III**) (41%), m.p. 259—262° (decomp.) (*penta-acetate*, m.p. 173—174°), also obtained by hydrogenation of (**II**) and hydrolysis of the resulting oil. (**III**) and its derivatives differ from any products (amorphous) obtainable from quebracho powder. R. S. C.

Vitamin-*E*. XXXI. 3 : 5-Dinitrobenzazide as a reagent for preparation of derivatives of tocopherols. L. I. Smith and J. A. Sprung. **XXXII. 6-Hydroxy-3-acetoxy-2 : 4 : 5-trimethylbenzylacetoacetic ester and its transformation into chromene and chroman derivatives.** L. I. Smith and R. B. Carlin. **XXXIII. Synthesis of 6-hydroxychromans, including *α*-tocopherol.** L. I. Smith and H. C. Miller. **XXXIV. The three dimethylethyltocols.** L. I. Smith and W. B. Renfrow, jun. **XXXV. Behaviour of tocopherols at the dropping mercury electrode.** L. I. Smith, L. J. Spillane, and I. M. Kolthoff (*J. Amer. Chem. Soc.*, 1942, **64**, 433—434, 435—440, 440—445, 445—447, 447—451; cf. A., 1941, II, 287).—XXXI. 3 : 5 : 1-$(NO_2)_2C_6H_3{\cdot}CON_3$ [prep. from the acid chloride (prep. by PCl_5), m.p. 67—70°, by NaN_3 in AcOH at ≯45°], m.p. 105° (decomp.), in boiling PhMe gives 70—90% of alkyltocyl 3 : 4-dinitrophenylurethanes,

which are well suited for identification. α-, m.p. 145—147°, β-, m.p. 153—154°, and γ-*tocopheryl*, m.p. 143—145°, 2 : 2 : 5 : 7 : 8-*pentamethyl-*, m.p. 207—208°, 7 : 8-*dimethyl-5-ethyl-*, m.p. 46—48°, 5 : 8-*dimethyl-7-ethyl-*, m.p. 67—69°, and 5 : 7-*dimethyl-8-ethyl-tocyl*, m.p. 58—60°, 3 : 5-*dinitrophenylurethane* are described.

XXXII. Addition of $CHAcNa{\cdot}CO_2Et$–Et_2O to 2 : 3 : 4 : 6 : 5 : 1-$OH{\cdot}C_6Me_3(OAc){\cdot}CH_2Cl$–$Et_2O$ at room temp. gives *Et* α-2-*hydroxy-5-acctoxy*-3 : 4 : 6-*trimethylbenzylacetoacetate* (**I**), m.p. 136—137° [with $NHPh{\cdot}NH_2$,AcOH in hot EtOH gives a pyrazolone *derivative*, m.p. 208—209°. (decomp.); positive Folin test; no ppt. with $Cu(OAc)_2$; previously (A., 1939, II, 416) believed to be the $(OH)_2$-compound]. With $CHAcNa{\cdot}CO_2Et$–Et_2O at room temp. (4 weeks) or solid NaOH in Et_2O at room temp. (3 weeks), (**I**) gives 3-acetyl-6-acetoxy-5 : 7 : 8-trimethyl-3 : 4-dihydrocoumarin, but with a trace of H_2SO_4 in boiling Ac_2O gives *Et* 6-*acetoxy*-2 : 5 : 7 : 8-*tetramethyl-γ-chromene*-3-*carboxylate* (**II**), m.p. 132—133°, colourless if boiled (twice) with Raney Ni in EtOH. In boiling 60% H_2SO_4, (**I**) or (**II**) gives 6-*hydroxy*-2 : 5 : 7 : 8-*tetramethylchroman* (**III**), m.p. 142—143°. Boiling NaOH–aq. EtOH hydrolyses (**II**) to 6-*hydroxy*-2 : 5 : 7 : 8-*tetramethyl-γ-chromene*-3-*carboxylic acid* (**IV**), m.p. 230—231° (decomp.) [*Et* ester, m.p. 173—175°, prepared by HCl–EtOH, yields (**II**)], the *Ac* derivative, m.p. 244—245° (decomp.), of which by way of the Ag salt regenerates (**II**). With a little Cu chromite in quinoline at 200° (later 220°), (**IV**) gives 2 : 5 : 3 : 4 : 6 : 1-$OH{\cdot}C_6Me_3{\cdot}[CH_2]_2{\cdot}COMe$ (or the OH-chroman), m.p. 122—124° (John *et al.*, A., 1940, II, 101, m.p. 122°), converted by H_2–Raney Ni in EtOH at 150°/1600 lb. into (**III**). Pure (**II**) with H_2–Raney Ni in EtOH at 125°/1300 lb. gives *Et* 6-*acetoxy*-2 : 5 : 7 : 8-*tetramethylchroman*-3-*carboxylate*, m.p. 76—77°, and thence (NaOH–EtOH–H_2O) 6-*hydroxy*-2 : 5 : 7 : 8-*tetramethylchroman*-3-*carboxylic acid*, m.p. 210—212° (decomp. from 205°) (*Ac* derivative, m.p. 199°; *Et* ester, m.p. 99°). The peculiarities of derivatives of *o*-$OH{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}COMe$ [*e.g.*, (**I**) probably exists at least partly as *Et* 2-*hydroxy*-6-*acetoxy*-2 : 5 : 7 : 8-*tetramethylchroman*-3-*carboxylate*] and the mechanism of their reactions are discussed.

XXXIII. Prep. of, successively, 1 : 2 : 3 : 5 : 6 : 4-$O{:}C_6Me_3Br{:}O$, 1 : 4 : 2 : 3 : 5 : 6-$(OH)_2C_6Me_3Br$ [*(CH$_2$Ph)$_2$ ether*, m.p. 144·5—146°, gives no Grignard reagent], RBr [R = $(OMe)_2C_6Me_3$ here and below], MgRBr (gives RCO_2H, m.p. 98—101°), $R{\cdot}[CH_2]_2{\cdot}OH$ (**V**), m.p. 73·5—75° (by $SOCl_2$–C_5H_5N or –Et_2O, not other methods), β-3 : 6-*dimethoxy*-2 : 4 : 5-*trimethylphenylethyl chloride* (**VI**), m.p. 60·5—61·5°, and (by PBr_3) *bromide*, m.p. 66—67°, is described. The Mg derivative (prep. from Mg activated by EtBr) of (**VI**) with $COMeR'$ (R' = Me, Et, Pr^{α}, or Bu^{β}) in Et_2O gives carbinols, converted by HBr–AcOH into 6-hydroxy-2 : 2 : 5 : 7 : 8-pentamethyl-, 6-*hydroxy*-2 : 5 : 7 : 8-*tetramethyl*-2-*ethyl-*, m.p. 60·5—62·5° (3 : 5-*dinitrophenylurethane*, m.p. 200—201·5°), -n-*propyl-*, m.p. 57—59°, and -iso*butyl-*, m.p. 42·5—44·5° (3 : 5-*dinitrophenylurethane*, m.p. 188—190°), *-chroman*, respectively. With $Bu^{\beta}{\cdot}[CH_2]_2{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}COMe$ (prep. from phytol by CrO_3, followed by O_3, described), RMgCl gives an oily carbinol (and αδ-*di*-3 : 6-*dimethoxy*-2 : 4 : 5-*trimethylphenylbutane*, m.p. 160—161°), which by cyclisation by HBr–AcOH–N_2 and then treatment with NaOEt–EtOH–N_2 gives α-tocopherol, which is best purified by Tishler and Wendler's method and is shown to be then identical chemically, physically, and biologically with the natural product, thus confirming the structure of the latter. $CH_2R{\cdot}CN$ is not reduced by $SnCl_2$–HCl–Et_2O (gives ? the amide, m.p. 195—202°) but yields successively $CH_2R{\cdot}CO_2H$, $CH_2R{\cdot}CO_2Et$, and (**V**). $CH_2R{\cdot}MgCl$ is formed in 57% yield, 19% of coupling to αβ-*di*-3 : 6-*dimethoxy*-2 : 4 : 5-*trimethylphenylethane*, m.p. 170—171°, also occurring. *Duroquinol Me_2 ether* (prep. by Me_2SO_4–KOH–MeOH), m.p. 112—115°, is described. $CMe_2Br{\cdot}CHBr{\cdot}OEt$ (prep. from $Pr^{\beta}CHO$ outlined) does not couple with $CH_2R{\cdot}MgCl$.

XXXIV. Condensation of the appropriate dimethylethylquinol with phytol by $ZnCl_2$ in AcOH at 125—130°, subsequent treatment with KOH–MeOH, and then distillation at 185—190°/10^{-5} mm. gives 60—75% of 7 : 8-*dimethyl*-5- (**VII**), 5 : 8-*dimethyl*-7- (**VIII**), and 5 : 7-*dimethyl*-8-*ethyltocol* (**IX**) (for 3 : 5-dinitrophenylurethanes see above), which are in general similar but show minor differences in physical properties. Biologically (**VIII**) is the least active, but all are less active than α-tocopherol.

XXXV. Polarograms are recorded for α-, β-, and γ-tocopherol, (**VII**), (**VIII**), (**IX**), the Me_4 analogue, and 4-hydroxy-3 : 5 : 6-trimethyl-1-ethyl-1 : 2-dihydrobenzfuran in 75% EtOH containing $NH_2Ph,HClO_4$ or $HClO_4$. The oxidation mechanism of Smith *et al.* (A., 1941, I, 270) is confirmed. (**VII**), (**VIII**), (**IX**), and α- (in presence of β- and γ-)tocopherol can be determined polarographically.

R. S. C.

Coumarins. I. Condensation of 4-acylresorcinols with ethyl acetoacetate in presence of anhydrous aluminium chloride. II. Condensation of substituted resacetophenones with ethyl acetoacetate in presence of aluminium chloride. C. V. Deliwala (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 133—134).—I. Respropiophenone (**I**), resbutyrophenone, 2 : 4-$(OH)_2C_6H_3{\cdot}CO{\cdot}CH_2Ph$, and 4-*p*-toluoylresorcinol condense with $CH_2Ac{\cdot}CO_2Et$ in $PhNO_2$ at 120—130° to 5-hydroxy-6-acylcoumarins. The constitution of 5-*hydroxy*-6-*propionyl*-4-*methylcoumarin*, from (**I**) is established by its formation by the Fries transformation of 5-propionoxy-4-methylcoumarin and by the production of 2′ : 3′ : 4-*trimethylchromono*-7′ : 8′ : 6 : 5-*pyrone*, m.p. 241—242°, by Kostanecki acetylation.

II. 5-Ethyl- and 5-bromo-resacetophenone condense with $CH_2Ac{\cdot}CO_2Et$ in presence of $AlCl_3$ to 5-*hydroxy*-6-*acetyl*-4-*methyl*-8-*ethyl*- and 8-*bromo*-5-*hydroxy*-6-*acetyl*-4-*methyl-coumarin* respectively; 5-nitro-, 5-carbomethoxy-, 5-acetyl-, and 5-benzyl-coumarin do not react. H. W.

Chromones of the naphthalene series. Transformation of *o*-aroyloxyacetoarones into *o*-hydroxydinaphthoylmethanes. V. V. Ullal, R. C. Shah, and T. S. Wheeler (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 118—119; cf. A., 1941, II, 21).—5-*Nitro*-4-*methoxy*-2-*benzoyloxyacetophenone*, m.p. 133°, obtained from nitropæonol (**I**), BzCl, and C_5H_5N, is converted by NaOEt into (**I**) and BzOH. Similarly 5-*nitro*-4-*methoxy*-2-1′-*naphthoyloxyacetophenone*, m.p. 146—148°, gives (**I**) and α-$C_{10}H_7{\cdot}CO_2H$. The presence if NO_2 appears to prevent completely the migration of the acyl group. 2-*Cinnamoyloxy*-1-*acetonaphthone*, m.p. 127—128°, and NaOEt afford 2-styryl-5 : 6-benzochromone, m.p. 197—198°. H. W.

[Structure of cannabidiol.] XIII. Tetrahydrocannabinol homologues and analogues with marihuana activity. R. Adams, S. Loewe, C. M. Smith, and W. D. McPhee (*J. Amer. Chem. Soc.*, 1942, **64**, 694—697; cf. A., 1941, II, 374).—Figures in parentheses below are potencies (dog) relative to 3′ : 4′ : 5′ : 6′-tetrahydrocannabinol. Dog-ataxia tests do not parallel Gayer tests on rabbits but correspond with reponse in man. Pulegone and the appropriate 5-alkylresorcinol in boiling $POCl_3$–C_6H_6 give H_4-compounds in which the 5″-alkyl is Pr^{α}, b.p. 160—163°/0·3 mm., α_D +78—94° (0·24), Bu^{α}, b.p. 147—150°/0·08 mm., α_D +71—80° (0·25±0·1), *amyl*, b.p. 190—200°/2·0 mm., α_D +72—77° (0·58±0·12), n-*hexyl*, b.p. 180—186°/0·3 mm., α_D +61—79° (1·22±0·12), n-*heptyl*, b.p. 184—186°/0·15 mm., α_D +54—79° (1·15±0·15), n-*octyl*, b.p. 177—182°/0·4 mm., α_D +50—80°(1·37±0·25), and n-*nonyl*, b.p. 190—200°/0·01 mm., α_D +55—68° (0·20), reduced (H_2–PtO_2–AcOH or H_2–Raney Ni in abs. EtOH at 75—100°/35—60 atm.) to the H_6-compounds, in which the 5″-alkyl is Pr^{α}, b.p. 161—165°/0·3 mm., α_D +14—24° (0·20), Bu^{α}, b.p. 173—176°/0·06 mm., α_D +16—18° (0·15), *amyl*, b.p. 179—183°/0·5 mm., α_D +2—9° (0·64±0·10), n-*hexyl*, b.p. 183—186°/0·3 mm., α_D +6·9° (0·78±0·22), n-*heptyl*, b.p. 187—193°/0·3 mm., α_D +7—10° (0·83±1·7), and n-*octyl*, b.p. 206—210°/0·1 mm., α_D +7—8° (0·25). 3-*Hydroxy*-2 : 2 : 5′-*trimethyl*-5″-n-*propyl-*, b.p. 158—160°/0·3 mm. (0·26±0·3), -*butyl-*, b.p. 165—167°/0·5 mm. (0·37±0·06), -*hexyl-*, b.p. 200—209°/3 mm. (1·86±0·37), -*heptyl-*, b.p. 186—187°/0·3 mm. (0·83±0·13), and -*octyl-*, b.p. 187—197°/0·2 mm. (0·24±0·06), -3 : 4 : 3′ : 4′ : 5′ : 6′-*hexahydro*-3 : 4 : 5 : 6-*dibenzpyran* (*A*) are described. The following potencies are also recorded : *n*-amyl analogue of (*A*) 0·51±0·08; tetrahydrocannabinol, $[\alpha]_D^{27}$ various, −126° to −265°, 6·5±0·65 to 9·3±2·9 (max. for $[\alpha]_D^{27}$ −165°); hexahydrocannabinol, $[\alpha]_D^{27}$ −70°, 3·0±0·43; crude hemp extracts 0·003—0·13; purified red oil 1·24; highly purified red oil 4·33. R. S. C.

Dibenzopyrans.—See B., 1942, II, 220.

Preparation of β-keto-amines by the Mannich reaction. F. F. Blicke and J. H. Burckhalter (*J. Amer. Chem. Soc.*, 1942, **64**, 451—454).—COPhMe (1), paraformaldehyde (**I**) (equiv. to 1·2 CH_2O), and NH_2Me,HCl in boiling abs. EtOH give $COPh{\cdot}[CH_2]_2{\cdot}NHMe,HCl$ (**II**) (29%), m.p. 140—142° (lit. 139—141°), and $(COPh{\cdot}[CH_2]_2)_2NMe,HCl$ (**III**) (34%), m.p. 161—162°. Distillation of (**III**) in steam gives (**II**) (78%) and $COPh{\cdot}CH{:}CH_2$. In aq. NaOH at 30°, (**III**) gives NH_2Me and $(COPh{\cdot}[CH_2]_2)_2NMe$ (**IV**), probably by decomp. to $COPh{\cdot}CH{:}CH_2$ and NH_2Me since these compounds in EtOH at room temp. give (**IV**). 2-Acetylthiophen with (**I**) and NH_2Me,HCl gives *di-γ-keto-γ*-2-*thienyl*-n-*propylmethylamine* (61%), m.p. 146—148° (*hydrochloride*, m.p. 185—186°), generally stable when distilled in steam but sometimes giving 2-thienyl vinyl ketone (see below). COPhMe, (**I**), and *acetmethylamide semihydrochloride*, m.p. 87—89°, in boiling abs. EtOH give (**III**). COPhMe, CH_2O, and $NHEt_2$,HCl give *β-diethylaminopropiophenone hydrochloride* (45%), m.p. 108—110° (picrate, m.p. 115—116°), which when distilled at 18 mm. gives $COPh{\cdot}CH{:}CH_2$ (80%). 2-Propionylthiophen, CH_2O, and $NHMe_2$,HCl give *β-dimethylisobutyrylthiophen hydrochloride* (60%), m.p. 154—156°, converted by distillation in steam into 2-α-*methylacrylothiophen* (71%), b.p. 118—120°/19 mm. (gives 1-*phenyl*-3-2′-*thienyl*-4-*methylpyrazoline*, m.p. 81—83°). 2-β-Dimethylamino- (**V**), m.p. 178—179° (lit. 172°), 2-β-piperidino-, m.p. 201—202° (lit. 199°), and 2-β-*diethylamino-*, m.p. 116—117°, *-propionylthiophen hydrochloride* are also described. (**V**) yields as above 2-*thienyl vinyl ketone*, b.p. 108—110°/12 mm. R. S. C.

Cleavage of the ethylene linkage by the action of sulphur. A. Schönberg and (Miss) W. Asker (*J.C.S.*, 1942, 272—274).—Dithioxanthylen (**I**), diflavylen, and dithioflavylen (**II**) with S at ~280° give the corresponding thioketones. A theory based on resonance is put forward to explain these reactions. Dixanthylen, (**I**), (**II**), αα′α″α‴-tetraphenyl-γγ′-dithiopyrylen and its Cl-derivative are obtained by treating the corresponding ketone with $SOCl_2$, followed by Cu-bronze. In the case of (**II**), an intermediate compound, m.p. 120°, is isolated. F. R. S.

Synthetic mydriatics. II. F. F. Blicke and C. E. Maxwell (*J. Amer. Chem. Soc.*, 1942, **64**, 431—433; cf. A., 1942, II, 224).—The following are prepared by standard methods. β-Piperidinoethyl benzoate hydrochloride, m.p. 170—171°, 1-*naphthoate hydrochloride*, m.p. 169—170°, phenylacetate hydrochloride, m.p. 145—146° (lit. 139°), *phenylglyoxylate hydrochloride*, m.p. 122—123°, *diphenylacetate hydrochloride*, m.p. 153—154°, α-*hydroxy*-n-*octoate hydrochloride*, m.p. 141—143°, *hexahydromandelate hydrochloride*, m.p. 180—181°, *mandelate hydrochloride*, m.p. 159—160°, 1-*hydroxyhexahydrobenzoate hydrochloride*, m.p. 201—202°, α-*naphthylglycollate hydrochloride**, m.p. 157—158°, β-*hydroxy*-α-*phenylpropionate methobromide*†, m.p. 127—128°, *dicyclohexylglycollate hydrochloride*†, m.p. 229—230° (corresponding *methobromide**, m.p. 216—217°), *diphenylglycollate acetate methobromide**, m.p. 220—221°, α-*methoxy*-, m.p. 178—179°, and α-*chloro-diphenylacetate hydrochloride**, m.p. 145—146°, 9-hydroxyfluorene-9-carboxylate, m.p. 136—137° (*hydrochloride**, m.p. 345—348°), and *mandelate acetate methobromide*, m.p. 141—142°; γ-dimethylamino-ββ-dimethyl-*n*-propyl mandelate acetate hydrochloride, m.p. 182—183° (lit. 179°), and 1-*hydroxyhexahydrobenzoate hydrochloride*, m.p. 174—175°. Esters marked * are slightly and those marked † strongly mydriatic; the others are inactive. R. S. C.

Synthesis of 7-amino-6-methoxyquinoline. V. M. Radionov and L. V. Antik (*J. Gen. Chem. Russ.*, 1941, **11**, 423—424).—2-Nitro-4-aminoanisole gives, by the Skraup reaction, a mixture of 5- and 7-nitro-6-methoxyquinoline (**I**), which were separated by crystallisation from ether. (**I**) is reduced (Fe and AcOH) to 7-*amino*-6-*methoxyquinoline*, m.p. 169—170·5°. N. G.

Structure of hydrogen cyanide. [Pyridine and quinoline thio- and seleno-cyanates.]—See A., 1942, I, 246.

Chemotherapeutic studies in acridine series. VIII. Chloroaminoacridines. F. R. Bradbury and W. H. Linnell (*Quart. J. Pharm.*, 1942, **15**, 31—40; cf. A., 1940, II, 331).—Condensation of 4 : 2 : 1-NO_2·C_6H_3Cl·CO_2Na with *o*-C_6H_4Cl·NH_2 yields 2′-*chloro*-5-*nitrodiphenylamine*-2-*carboxylic acid*, m.p. 254—256°, which on ring-closure (PCl_5) gives 9-*chloro*-2-*nitroacridone*, m.p. 340°, reduced ($SnCl_2$) to the NH_2-compound, m.p. 310—312° (decomp.), and thence (Na–Hg) the *-acridine*, m.p. 125° (*monohydrochloride*). 4′-*Chloro*-4-*nitrodiphenylamine*-2-*carboxylic acid*, m.p. 285° (decomp.), 7-*chloro*-3-*nitro*-, m.p. >320°, and -3-*amino-acridone*, m.p. >310°, and 7-*chloro*-3-*aminoacridine*, m.p. 208—209 (*monohydrochloride*), are similarly produced from 5 : 2 : 1-NO_2·C_6H_3Cl·CO_2K and *p*-C_6H_4Cl·NH_2, whilst with *o*-C_6H_4Cl·NH_2 the same series of reactions give 2′-*chloro*-4-*nitrodiphenylamine*-2-*carboxylic acid*, m.p. 273—275° (decomp.), and 9-*chloro*-3-*nitroacridone*, m.p. >320°. This is not reduced by $SnCl_2$, but Na–Hg yields 9-*chloro*-3-*aminoacridine*, m.p. 172—173° (*mono*- and *di-hydrochloride*). 7-*Chloro*-2-*amino-acridone*, m.p. >330°, and -*acridine*, m.p. 240° (decomp.) (*monohydrochloride*), are similarly prepared from 7-chloro-2-nitroacridone. When tested against *B. coli*, *Staphylococcus*, *Streptococcus*, and *Ps. pyocyanea* these Cl-compounds have very little activity when compared with the parent amines, and 6- and 7-chloro-2-aminoacridine show only a moderate activity. It is concluded that introduction of Cl depresses bactericidal activity and that position isomerism has no effect in this series. J. N. A.

Benzacridones.—See B., 1942, II, 223.

Hypnotic action of 2-iminobarbituric acids [dialkylmalonylguanidines]. R. Barré and A. Jacques (*Rev. Canad. Biol.*, 1942, **1**, 454—463; see also A., 1942, III, 549).—2-Thio-5 : 5-diethylbarbituric acid [from $CEt_2(CO_2Et)_2$ (**I**) and $CS(NH_2)_2$ in EtOH–NaOEt] with NH_3 (in EtOH at 80°), NH_2Bu (heat), and NH_2Ph (at 120—130°) gives 2-imino- [better obtained from (**I**) and guanidine carbonate in EtOH–NaOEt], 2-butylimino-, m.p. 159—160°, and 2-anilo-, m.p. 251—252°, -5 : 5-diethylbarbituric acid, respectively. 2-Thio-, m.p. 175—176°, and 2-imino-, decomp. >300°, -5-ethyl-5-*iso*amyl- and 2-imino-5 : 5-dipropyl-barbituric acids are similarly prepared. H. B.

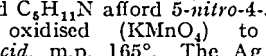
Thiobarbituric acids.—See B., 1942, III, 142.

Pyrazolones.—See B., 1942, II, 187.

Preparation of 4(5)-hydroxymethylglyoxaline. W. J. Darby, H. B. Lewis, and J. R. Totter (*J. Amer. Chem. Soc.*, 1942, **64**, 463—464).—Prep. of 4(5)-hydroxymethylglyoxaline picrate in 61—64% yield from fructose, CH_2O, basic Cu carbonate, and aq. NH_3 is described. It gives also picrates of two other glyoxaline derivatives, possibly including 4(5)-[*d*-arabino]tetrahydroxybutylglyoxaline (cf. Weidenhagen *et al.*, A., 1937, II, 211; Akabori *et al.*, A., 1940, II, 314). R. S. C.

Constitution of purine nucleosides. X. New synthesis of xanthine and attempted syntheses of xanthine glucosides from glyoxalines. W. E. Allsebrook, J. M. Gulland, and L. F. Story (*J.C.S.*, 1942, 232—236).—The hydrochloride of Me 4(5)-aminoglyoxaline-5(4)-carboxylate with KCNO gives *Me* 4(5)-*ureidoglyoxaline*-5(4)-*carboxylate*, m.p. 213° (*hydrochloride*, m.p. 208°), hydrolysed (NaOH) to the *acid*, decomp. without m.p., which when heated with HCl affords xanthine. 4(5)-*Nitro*-5(4)-3′ : 4′-*methylenedioxystyrylglyoxaline* has m.p. 288° (decomp.), and the *methosulphate* of 4(5)-nitro-5(4)-methylglyoxaline has m.p. 143—144°. The glycosidyl radical could not be introduced into a suitable glyoxaline in a suitably determined position because tetra-acetobromoglucose (**I**) does not react with the Ag salt of the Me ester (**II**) of 4(5)-nitroglyoxaline-5(4)-carboxylic acid or 4(5)-nitro-5(4)-styrylglyoxaline. MeI and the Ag salt of (**II**) give *Me* 4-*nitro*-1-*methylglyoxaline*-5-*carboxylate*, m.p. 128—129°, hydrolysed to the acid, also obtained by oxidation ($KMnO_4$) of 4-*nitro*-5-*styryl*-1-*methylglyoxaline*, m.p. 150—151° (from 4-nitro-1 : 5-dimethylglyoxaline and PhCHO). 5-Nitro-1 : 4-dimethylglyoxaline, PhCHO, and $C_5H_{11}N$ afford 5-*nitro*-4-*styryl*-1-*methylglyoxaline*, m.p. 214—215°, oxidised ($KMnO_4$) to 5-*nitro*-1-*methylglyoxaline*-4-*carboxylic acid*, m.p. 165°. The Ag salt of 5(4)-nitroglyoxaline-5(4)-carboxylamide with MeI gives 5-*nitro*-1-*methylglyoxaline*-4-*carboxylamide*, m.p. 234°; the Ag salt of this does not react with (**I**). F. R. S.

Condensation of *o*-phenylenediamine with ethyl acetoacetate. W. A. Sexton (*J.C.S.*, 1942, 303—304).—Condensation of *o*-$C_6H_4(NH_2)_2$ with $CH_2Ac·CO_2Et$ in presence of HCl gives Et β-2-aminoanilinocrotonate, cyclised to 2-methylbenziminazole. In boiling xylene solution, condensation affords a *compound*,



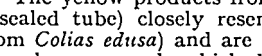
m.p. 121°, and *benziminazole*-2-*acetone*, m.p. 148°, which is also obtained by reduction (Fe, HCl, EtOH) of *acetoacet*-*o*-*nitroanilide*, m.p. 65°. F. R. S.

Constitution of yeast-ribonucleic acid. V. Synthesis of yeast-adenylic acid. G. R. Barker and J. M. Gulland (*J.C.S.*, 1942, 231—232).—Adenosine and $Ba(OH)_2$–$POCl_3$–Et_2O give yeast-adenylic acid (adenosine 3-phosphate). F. R. S.

Pterins [rhodopterin]. (Sir) F. G. Hopkins (*Proc. Roy. Soc.*, 1942, **B**, **130**, 359—379).—*Rhodopterin* (**I**) [formerly named lepidoporphyrin (cf. A., 1896, ii, 198)] is formed in 12·2—33% yield by oxidation of various (yellow) pterins (*A*) (but not leucopterin) with atm. O_2 in 0·1N-H_2SO_4 at ~85°, whereby no CO_2 or NH_3 is produced, and is obtained cryst. by using a low concn. of (*A*) and (apparently) a slow supply of O_2 at the start, or by carrying out the oxidation in presence of a trace of cryst. (**I**). Formation of (**I**) does not occur at p_H 6 but is evident at 4·6; production proceeds normally, however, in 20% (vol.) H_2SO_4. Erythropterin (Schöpf *et al.*, A., 1936, 1260) is probably the precursor of (**I**), which is probably not produced from "classical" xanthopterin (**II**). The formation of some (**I**) from (**II**) (probably not pure) is noted; this occurs rapidly if the (**II**) has been treated with boiling aq. $Ba(OH)_2$ (cf. Schöpf *et al.*, A., 1939, II, 392) and it is considered that the stability of (**II**) is thereby lessened in at least one direction. (**I**) is insol. in org. solvents, H_2O, or <4% H_2SO_4, slightly sol. in aq. NH_3, but sol. in conc. H_2SO_4 without decomp.; it is freely sol. in aq. NaOH or KOH but is thereby decomposed. Solutions in H_2SO_4 show well-defined absorption bands at 548 and 504 mμ. (**I**) is oxidised by H_2O_2 in 2N-NH_3 to colourless products. Concordant analytical vals. (quoted) for various preps. of (**I**) were not obtained. Details for the isolation of (*A*) from the wings of pierid butterflies are given; (*A*) are sol. in warm $(CH_2·OH)_2$. The yellow products from uric acid and dil. H_2SO_4 at 190—195° (sealed tube) closely resemble pterins (*e.g.*, the mixed pigments from *Colias edusa*) and are oxidised [as for (*A*) but more slowly] to purple compounds which differ from (**I**) by their insolubility in cold 20% H_2SO_4. H. B.

Pyrazolones and oxazolones.—See B., 1942, II, 207.

Reactions of benzthiazole derivatives. III. Interaction of 1-thiolbenzthiazoles and alcohols. W. H. Davies and W. A. Sexton (*J.C.S.*, 1942, 304—307).—When heated with MeOH or EtOH in the presence of catalysts, 1-thiolbenzthiazoles afford benzthiazole derivatives, which it is suggested are derived by loss of H_2O, H_2S, or RSH from a labile hypothetical additive product,

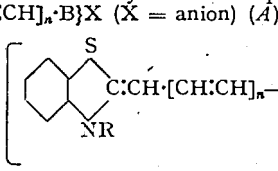


1-*Methoxybenzthiazole*, m.p. 34—35°, obtained from the corresponding Cl-derivative (cf. Hunter *et al.*, A., 1936, 214), is isomerised to 2-methylbenzthiazolone, and the reaction is not catalysed by I. F. R. S.

Benzthiazoles.—See B., 1942, II, 223.

Cyanine dyes.—See B., 1942, II, 220.

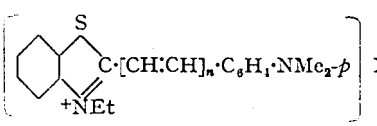
Colour and constitution. V. Absorption of unsymmetrical cyanines. Resonance as a basis for a classification of dyes. L. G. S. Brooker, G. H. Keyes, and W. W. Williams (*J. Amer. Chem. Soc.*, 1942, **64**, 199—210; cf. A., 1942, II, 153).—Among cyanine, thiacyanine, and similar dyes the absorption max. of the mixed dye, A:CH·[CH:CH]$_n$·B}X (X = anion) (*A*) approaches more closely the



(*B.*)

arithmetical mean of the max. of the dyes, A:CH·[CH:CH]$_n$·A}X and B:CH·[CH:CH]$_n$·B}X, the more nearly equal are the basicities of

A and B; the difference between the max. of (*A*) and this arithmetical mean is termed the deviation. In the series (*B*; R = Et) the deviation calc. from $\lambda_{max.}$ is very small; calc. from wave nos. it is discernible but still small. The benzthiazole nucleus of (*B*) is the less basic; negative substituents in this nucleus lower the basicity and lead to large deviations, relative effects being 5-NO_2 > 2-*o*-$NO_2{\cdot}C_6H_4$ > 2-Ph. When the deviation is nil, absorption max. of successive members of a series differ by const. amounts but with marked deviations these differences become smaller as *n* increases; *i.e.*, series in which basicities of *A* and *B* differ tend to a limiting val. of the absorption max. with higher *n*. This tendency is termed "convergence." It parallels the deviation in (*B*), *i.e.*, no convergence when R = Et, rising to a max. when R = H and a 5-NO_2 is present. In the series (*C*), the degeneracy is decreased by the aromatic nature of C_6H_4 tending to stabilise the form of (*C*) shown; this effect is lessened by negative substituents in the benzthiazole ring which decrease the stability of the quaternary thiazolinium form, so that the 5-NO_2-derivatives of (*C*) show less deviation and are more convergent [*i.e.*, the opposite effect to that with (*B*)].



(*C*.)

Polyene dyes are an extreme case of non-degeneracy but differ from cyanines in that interchange of $^+CHR{\cdot}[CH{:}CH]_n{\cdot}C^-HR$ and $^-CHR[{:}CH{\cdot}CH{:}]_{n+1}{\cdot}CHR$ involves a shift of two electrons and the non-polar form is more stable than the polar forms.

Figures in parentheses below are absorption max. (A.) in $MeNO_2$. Deviations (A.) are denoted by *D*, and increases per unit increase of *n* by *V* (A.). 2-Phenylbenzthiazol-1-one and P_2S_5 in boiling xylene give 1-*thion*-2-*phenylbenzthiazoline*, m.p. 98—99°, converted by *p*-$C_6H_4Mc{\cdot}SO_3Me$ at 100° into 1-*methylthiol*-2-*phenylbenzthiazolinium* p-*toluenesulphonate* (**I**), m.p. 176—179°, which with $CH_2(CO_2Et)_2$ and NEt_3 in EtOH gives 2-*phenyl*-1-*dicarbethoxymethylenebenzthiazoline*, m.p. 178—179°. In boiling 20% HCl this yields 2-*phenyl*-1-*methyl*- (**II**), m.p. 209—210°, converted by NPh:CH·NHPh in Ac_2O into 2-*phenyl*-1-β-*acetanilidovinyl*-*benzthiazolium iodide* (**III**), m.p. 208—209°. 5-Nitro-1-methylbenzthiazole [prep. by HNO_3 (*d* 1·49) at room temp.], m.p. 166—167° (lit. 175°) (structure proved by conversion into the 6-Cl-derivative), and Et_2SO_4 at 120—125° etc. give the *cthiodide* (**IV**), m.p. 254—255°, and thence the ethochloride (**V**). Lepidine ethiodide (**VI**) gives, as above, 4-β-anilino- and thence 4-β-acetanilido-vinylquinoline ethiodide (**VII**), and with NHPh·CH:CH·CH:NPh,HCl (**VIII**) in Ac_2O gives 4-δ-*acetanilido*-$\Delta^{\alpha\gamma}$-*butadienylquinoline ethiodide* (**IX**), m.p. 121—123°. (**I**), (**VI**), and NEt_3 in EtOH give 2-*phenyl*-1′-*ethylthia*-4′-*cyanine iodide* (*B*; *n* = 0; R = Ph), m.p. 277—279° (5030; *D* 70). (**III**) and (**VI**) in C_5H_5N give 2-*phenyl*-1′-*ethylthia*-4′-*carbocyanine perchlorate* (*B*; *n* = 1; R = Ph), m.p. 241—243° (6265; *D* 85; *V* 1235). (**II**), (**IX**), and NEt_3 in EtOH give 2-*phenyl*-1′-*ethylthia*-4′-*dicarbocyanine perchlorate* (*B*; *n* = 2; R = Ph), m.p. 170—171° (7200; *D* 180; *V* 935). 2-*o*-Nitrophenyl-1-methylbenzthiazolium perchlorate (**X**) with (*a*) quinoline ethiodide and KOH–EtOH, (*b*) (**VII**)–C_5H_5N, or (*c*) (**IX**)–NEt_3–EtOH gives 2-o-*nitrophenyl*-1′-*ethylthia*-4′-*cyanine perchlorate* (*B*; R = *o*-$NO_2{\cdot}C_6H_4$; *n* = 0), m.p. 284—286° (4985), -4′-*carbocyanine perchlorate*, m.p. 223—225° (6150; *D* 225; *V* 1165), and -4′-*dicarbocyanine perchlorate*, m.p. 195—196° (6810; *D* 580; *V* 660), respectively. With 4-iodoquinoline ethiodide–NEt_3–EtOH, (**VII**)–C_5H_5N, or (**IX**)–NEt_3–EtOH, (**V**) gives 5-*nitro*-2 : 1′-*diethylthia*-4′-*cyanine iodide*, m.p. 307—309° (5045; *D* 160), -4′-*carbocyanine iodide*, m.p. 299—301° (6170; *D* 275; *V* 1125), and -4′-*dicarbocyanine iodide*, m.p. 218—220° (6800; *D* 675; *V* 630). $CH_2(CO_2H)_2$ and (**I**) in C_5H_5N give 2 : 2′-*diphenylthiacyanine iodide*, m.p. >315° (4290). With $CH_2(CO_2H)_2$ or OEt·CH:CH·CH(OEt)$_2$, (**II**) in C_5H_5N gives 2 : 2′-*diphenylthia*-*carbo*-, m.p. 276—277° (5655), and -*dicarbo*-*cyanine iodide*, m.p. 226—228° (6650). 2 : 2′-*Di*-o-*nitrophenylthiadicarbocyanine perchlorate*, m.p. 257—258° (6700), is obtained from (**X**), NHPh·CH:CH·CH:NPh,HCl (**XI**), and NaOAc in Ac_2O. With $NPh_2{\cdot}NO$ or $CH(OEt)_3$ in Ac_2O, (**V**) gives 5 : 5′-*dinitro*-2 : 2′-*diethylthia*-*cyanine chloride*, m.p. 326—328° (4496 in MeOH), and -*carbocyanine chloride*, m.p. 278—280° (5900), respectively. (**IV**) and (**XI**) in C_5H_5N give 5 : 5′-*dinitro*-2 : 2′-*diethylthiadicarbocyanine iodide*, m.p. 274—276° (6905). 2-*Phenyl*-, m.p. 242—246° (5465; *D* 415; *V* 555), and 2-o-*nitrophenyl*-, m.p. 185—186° (5605; *D* 290; *V* 785), -1-p-*dimethylaminostyrylbenzthiazolium perchlorate* are prepared from (**II**) or (**X**), respectively, by *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ in EtOH; 5-*nitro*-1-p-*dimethylaminostyrylbenzthiazolium ethochloride*, m.p. 256—258° (5735; *D* 265; *V* 775), is obtained similarly from (**V**). *p*-$NMe_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CHO$ yields similarly 2-*phenyl*-1-δ-p-*dimethylaminophenyl*-$\Delta^{\alpha\gamma}$-*butadienylbenzthiazolium iodide*, m.p. 168—170° (5700; *D* 1075), 2-o-*nitrophenyl*-1-δ-p-*dimethylaminophenyl*-$\Delta^{\alpha\gamma}$-*butadienylbenzthiazolium perchlorate*, m.p. 221—222° (6390; *D* 465), and 5-*nitro*-1-δ-p-*dimethylaminophenyl*-$\Delta^{\alpha\gamma}$-*butadienylbenzthiazolium ethobromide*, m.p. 220—222° (6390; *D* 465). 5-, m.p. 291—293° (5800 in MeOH; *D* 140), and 6′-*nitro*-2 : 1′-*diethylthia*-2′-*carbocyanine iodide*, m.p. 293—295° (6000 in MeOH; *D* —50), are obtained from (*a*) 2-β-acetanilidovinylquinoline ethiodide and (**V**) or (*b*) 1-β-acetanilidovinylbenzthiazole ethiodide and 6-*nitroquinaldine ethiodide* (**XII**), m.p. 220—223°, respectively, in C_5H_5N. $CH(OEt)_3$ and (**XII**) in C_5H_5N give 6 : 6′-*dinitro*-1 : 1′-*diethyl*-2 : 2′-*carbocyanine chloride*, m.p. 306—309° (6320 in MeOH). M.p. are corr.; those of salts are with decomp. R. S. C.

VII.—ALKALOIDS.

Synthesis of a structural analogue of pilocarpine. G. V. Tschelincev and V. A. Fisch (*J. Gen. Chem. Russ.*, 1941, **11**, 459—460).—α-Acetyl-α-4(5)-glyoxalinylmethylbutyrolactone [*hydrochloride*, m.p. 157°; *aurichloride*, m.p. 184—186° (decomp.)] was obtained by condensing 4(5)-chloromethylglyoxaline with sodio-α-acetyl-γ-butyrolactone. It did not show the physiological action of pilocarpine. N. G.

Erythroidine.—See B., 1942, II, 142.

Veratrine alkaloids. XIII. Dehydrogenation of protoveratrine. L. C. Craig and W. A. Jacobs (*J. Biol. Chem.*, 1942, **143**, 427—432; cf. A., 1941, II, 272).—The alkamine protoverinc is related in structure to cevine (cf. Poethke, A., 1938, II, 35). Protoveratrine and Se at 340° (in N_2) afford AcOH, CHMeEt·CO_2H, OH·CMeEt·CO_2H, 2 : 5-dimethylpyridine, 5-methyl-2-ethylpyridine, a base, C_6H_9ON (isolated as picrate, m.p. 114—117°), impure cevanthrol, m.p. 168—175°, and a trace of impure cevanthridine (picrate isolated). A. T. P.

Alkaloid *F*56, $C_{19}H_{15}O_2N(OMe)_4$, m.p. 207°, from *Corydalis montana*.—See A., 1942, III, 502.

VIII.—ORGANO-METALLIC COMPOUNDS.

Polymerisation of derivatives of aluminium trimethyl. N. Davidson and H. C. Brown (*J. Amer. Chem. Soc.*, 1942, **64**, 316—324).—Prep. of the following *compounds* is described: $AlMe_2{\cdot}NMe_2$, $AlMe_2{\cdot}PMe_2$ (**I**), $AlMe_2{\cdot}OMe$ (**II**), $AlMe_2{\cdot}SMe$ (**III**), $AlMe_2Cl$, and $AlMe_2Br$. All are volatile at high temp. and dimeric as vapours except (**I**) and (**II**) (trimeric). $\{AlMe_2Cl(Br)\}_2$ gives 1 : 1 additive compounds with Me_2O–NMe_3; (**III**) combines with NMe_3 but not with Me_2O; the others react with neither. The tendency to combine may run parallel with diminished polymerisation. Monomeric additive *compounds* of $AlMe_3$ with NMe_3, PMe_3, Me_2O, and Me_2S have been prepared. Their stabilities are in the order NMe_3,$AlMe_3$ > PMe_3,$AlMe_3$ > Me_2O,$AlMe_3$ > Me_2S,$AlMe_3$, but only Me_2S,$AlMe_3$ is measurably dissociated as a vapour at 150°/40 mm. Bridged structures are proposed for the high-stability compounds. Additive *compounds* of $AlMe_3$ with $NHMe_2$ and $PhMe_2$ have been isolated. $AlMe_2Cl$ is a stronger acid (Lewis' sense) than $AlMe_3$. BMe_3 and $AlMe_3$ do not combine. PMe_3 has m.p. −85·3° to −84·3°. Corr. v.p. vals. for Me_2S and MeSH are given. W. R. A.

Oxidation of bismuth triethyl. G. Calingaert, H. Soroos, and V. Hnizda (*J. Amer. Chem. Soc.*, 1942, **64**, 392—397).—With 1·3 O_2 at −25° $BiEt_3$ gives solids (*a*), *Bi diethyl ethoxide* (**I**), m.p. 116°, sublimes at 70—100°/1 mm., (?) OEt·BiO, and Bi_2O_3 (54 : 26 : 20 mol.-%), and liquids (*b*), Et_2O_2, Et_2O, and EtOH (53 : 14 : 33 mol.-%). With O_2 at −40° rising to 25°, (*a*) give OEt·BiO + B_2O_3 (77 : 23 mol.-%) and Et_2O + Et_2O_2 + EtOH (21 : 6 : 73 mol.-%). In both cases only a trace of gas (? C_2H_4) is evolved. The structure of (**I**) is proved by synthesis (49% yield) from $BiEt_2Br$ and NaOEt in hexane–EtOH at −40°. Oxidation of (**I**) gives products similar to those obtained from (*a*). Oxidation of $BiEt_3$ and (**I**) involves formation of unstable peroxides; thus, the reaction may be explosive and an unstable liquid (? $BiEt_3O_2$) is obtained from $BiEt_3$. R. S. C.

Reaction between organic bismuth compounds and monobasic organic acids. III. M. M. Koton (*J. Gen. Chem. Russ.*, 1941, **11**, 379—381).—$BiPh_3$ with propionic, lactic, butyric, α-hydroxybutyric, *iso*valeric, hexoic, benzoic, or stearic acid gives C_6H_6; $Bi(C_{10}H_7)_2$ with HCO_2H or AcOH gives $C_{10}H_8$. In each case the Bi basic salts or oxides are also formed. N. G.

Anhydrohydroxymercuri-5-chloro-2-hydroxydiphenyl.—See B., 1942, II, 187.

Mercuri-organic compounds. XVII. Synthesis of organic mercurials of the pyridine series by diazotisation. A. N. Nesmejanov and I. F. Lutzenko (*J. Gen. Chem. Russ.*, 1941, **11**, 382—385; cf. A., 1938, II, 208).—Hg^{II} 3-*pyridyl bromide* (**I**), and *iodide* (**II**), *HgPh* 3-*pyridyl* (**III**), and *Hg bis*-5-*bromo*-3-*pyridyl* (**IV**) were prepared from either 3-*amino*- (**V**) or 5-*bromo*-3-*amino*-*pyridine* (**VI**) by diazotisation and the subsequent action of Cu powder on the diazo-compounds. (**I**), m.p. 271·5—272°, and (**II**), m.p. 270° (decomp.), were obtained via the double salt $C_5H_4N{\cdot}N_2Cl,HgCl_2$; (**III**), m.p. 174—175°, was obtained from Hg 3-pyridyl chloride and $SnPhCl_3$, whilst (**IV**), m.p. 225—227°, was prepared through $C_5H_3BrN{\cdot}N_2Cl,HgCl_2$. Treatment of $C_5H_3ClN{\cdot}N_2Cl,HgCl_2$ (from 2-chloro-5-aminopyridine) did not produce the corresponding Hg C_5H_5N derivative. N. G.

Preparation of symmetrical organomagnesium compounds. J. Décomb (*Compt. rend.*, 1941, **213**, 179—181).—Symmetrical organomagnesium compounds (MgR_2) may be prepared according to $2(RMgX,Et_2O) \rightleftharpoons MgR_2 + MgX_2(Et_2O)_2$ by pptn. of Mg halide with dioxan. Analysis of the supernatant solution for residual halogen and Mg shows that the optimum amounts of dioxan are 1·25—1·5 mols. per mol. Mg, giving 50—94% of initial Mg as MgR_2. The best halides are chlorides (83—89%); bromides give 64—94% but aliphatic iodides are unsuitable. C. S.

Disproportionation of Pb_2R_6 compounds. G. Calingaert, H. Soroos, and H. Shapiro (*J. Amer. Chem. Soc.*, 1942, **64**, 462—463).—*Pb_2 hexa-methyl* or *-ethyl* at 100±5° (N_2) gives $PbMe_4$ 18, $PbMe_3Et$ 15, $PbMe_2Et_2$ 23, $PbMeEt_3$ 31, and $PbEt_4$ 13 mol.-%. Since $PbAlk_4$ is stable at 100° in absence of a catalyst, the formation of mixed compounds occurs before or during the decomp. of Pb_2R_6. R. S. C.

Reaction between lead tetraphenyl and monobasic organic acids. II. M. M. Koton (*J. Gen. Chem. Russ.*, 1941, **11**, 376—378; cf. A., 1939, II, 566; 1940, II, 199).—$PbPh_4$ when treated with some monobasic acids HX at 100°/2 hr. gives compounds $PbPh_2X_2$. The products had the following m.p.: *dipropionate*, 170—172°; *di-lactate*, 212—215 (decomp.); *dibutyrate*, 132—134°; *di-α-hydroxybutyrate*, 198—201° (decomp.); *diisovalerate*, 166—168°; *dibenzoate*, 231—232°. The *dihexoate* could not be cryst. The OH-acids reacted the most readily with $PbPh_4$. The yield of the $PbPh_2X_2$ salt fell with increasing chain-length. Stearic acid did not react. N. G.

Substitution of radicals in organometallic compounds of group IV. Substitution of radicals by iodine in compounds of the type SnR_4. Z. M. Manulkin (*J. Gen. Chem. Russ.*, 1941, **11**, 386—391; cf. A., 1935, 967).—The substitution by I of one or more alkyl groups in $SnMe_4$, $SnEt_4$, $SnPr^a_4$, $SnBu^a_4$, and $Sn(C_5H_{11}\text{-}iso)_4$ (prep. by Grignard reaction in Et_2O or xylene) leads first to compounds SnR_3I, viz., $SnMe_3I$, b.p. 69° 15 mm., $SnEt_3I$, b.p. 117—118°/15 mm., $SnPr^a_3I$, b.p. 140—141°/15 mm., $SnBu^a_3I$, b.p. 190°/25 mm., $SnI(C_5H_{11})_3$, b.p. 168°/4 mm. In the absence of solvent all the alkyl groups in $SnMe_4$ and $SnEt_4$ could be replaced by I, the first two stepwise, and the second two simultaneously, to give $SnMe_2I_2$, m.p. 44°, and $SnEt_2I_2$, m.p. 30—31°, or SnI_4. N. G.

IX.—PROTEINS.

New methods of preparative organic chemistry. VIII. Preparation of pure proteins. G. Schramm (*Angew. Chem.*, 1941, **54**, 7—14).—A review. W. McC.

Methods for the preparation of large protein crystals. K. Bailey (*Trans. Faraday Soc.*, 1942, **38**, 186—191).—Methods employing (1) salting out, (2) slow dialysis, and (3) slow cooling are described for obtaining large crystals of edestin, excelsin, castor-seed globulin, ovalbumin, and muscle-albumin. The albumins may be obtained in crystals 18—150 μ. long and 3—15 μ. wide, suitable for orientation by streaming. Water of crystallisation in edestin and excelsin is ~40%. F. L. U.

Carbon suboxide and proteins. V. Nature of the reaction. A. H. Tracy and W. F. Ross (*J. Biol. Chem.*, 1942, **142**, 871—879; cf. A., 1941, II, 89).—The free NH_2- and tyrosine phenolic groups of serum-albumin appear to have reacted completely with malonic acid (I) after addition of thrice the theoretical amount of C_3O_2, which, unlike keten, reacts with free NH_2- and tyrosine phenolic groups at approx. the same rate. (I), bound to tyrosyl phenolic groups, is labile even in the cold and rapidly hydrolysed under physiological conditions. Substituted tyrosine derivatives develop with the phenol reagent < the theoretical intensity of colour equiv. to their tyrosine content. H. W.

Alkaline hydrolysis of ovalbumin. R. C. Warner (*J. Biol. Chem.*, 1942, **142**, 741—756).—Determinations of NH_3, NH_2 (with HNO_2), and NH_2-acids (with ninhydrin) liberated by alkaline hydrolysis of ovalbumin show that the rate of formation of free NH_2-groups increases with increase in temp. (35—100°) and in alkali concn. (0·28—4·3N.). $Ba(OH)_2$ acts more rapidly and more completely than NaOH. With 4·3N-NaOH at 100° a secondary reaction results in decrease in formation of free NH_2-groups with increase in duration of hydrolysis. The amount of free NH_2-acid produced is < equiv. to the amount calc. from the results of the free NH_2 determinations. A theory which relates the rate of production of free NH_2-acids to the no. of peptide linkings hydrolysed accounts for the course of acid but not for that of alkaline hydrolysis. W. McC.

Formation of ammonia from proteins in alkaline solution. R. C. Warner and R. K. Cannan (*J. Biol. Chem.*, 1942, **142**, 725—739).—Determination of the amounts of NH_3 produced from cryst. ovalbumin (I), edestin, and β-lactoglobulin by NaOH (0·28—4·3N.) and $Ba(OH)_2$ (2·3N.) shows that unknown sources of NH_3 in addition to amide groups and arginine residues exist in these proteins. Only part of the NH_3 from these sources is liberated when acid hydrolysate of (I) is heated with NaOH. Probably NH_3 from the unknown sources is produced, not by decomp. of any NH_2-acid residue as such but by degradation of some part of the protein structure. The rate of production of this NH_3 is best accounted for by assuming that it is derived from two independent sources by reactions of the first order. W. McC.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Salvia carnosa (**Dougl.**). **II. Carnosol.** A. I. White and G. L. Jenkins (*J. Amer. Pharm. Assoc.*, 1942, **31**, 37—43).—*Carnosol* (I) (from *S. carnosa*; cf. A., 1942, III, 563), $C_{19}H_{26}O_4$, m.p. 219·5° (decomp.) [Me_2 derivative, m.p. 152·5—153·5° (hydrolysed by EtOH–NaOH to an acid, m.p. 140—160°); Ac_2 derivative, m.p. 165—166°; Bz_2 derivative, m.p. 172°], could not be hydrogenated (H_2–Pt-black under pressure) and gave no identifiable products on oxidation with neutral or alkaline $KMnO_4$. Distillation of (I) with Zn dust gave a liquid, $C_{14}H_{18}$, b.p. 298—300°, n_D^{25} 1·5584, dehydrogenated (S) to phenanthrene, whilst pyrolysis gave a cryst. solid, m.p. 160—162°. (I) is possibly a dihydroxyoctahydrophenanthrene derivative, for which a tentative partial structural formula is advanced. All m.p. are uncorr. F. O. H.

Chemical nature of actinomycin, an antimicrobial substance produced by *Actinomyces antibioticus*. S. A. Waksman and M. Tishler (*J. Biol. Chem.*, 1942, **142**, 519—528).—*Actinomycin A* (I), m.p. 250° (slow decomp.), $[\alpha]_D^{25}$ −320°±5° in EtOH, mol. wt. ~800, has been isolated as a red pigment from a soil organism, *A. antibioticus*. Out of 250 strains of actinomycetes tested, no other organism appears to produce this pigment. It contains C 59, H 6·8, N 13·35, and O 20·8%; it appears to be a polycyclic N compound. It exhibits characteristic absorption in the visible and ultra-violet regions. From its behaviour towards reducing agents, it appears to have a reversible oxidation-reduction system apparently of a quinone type. Reductive acetylation of (I) gives a *compound*, m.p. 241°, whereas acetylation in absence of Zn dust leads to a *substance*, m.p. 250°. (I) is an active bacteriostatic and bactericidal as well as fungistatic and fungicidal agent, the degree of activity varying with the nature of the organism. It is active in concn. of 1 : 10^8 against certain Gram-positive bacteria and is highly toxic to animals. H. W.

Biochemistry of micro-organisms. LXX. Stipitatic acid, $C_8H_6O_6$, metabolic product of *Penicillium stipitatum*, Thom. J. H. Birkinshaw, A. R. Chambers, and H. Raistrick (*Biochem. J.*, 1942, **36**, 242—251).—*P. stipitatum*, Thom, grown on Czapek–Dox medium, produces *stipitatic acid* (I), $C_8H_6O_5$, m.p. 302—304° (decomp.; darkens at 295°) [*diacetate*, m.p. 172·5° (Ac_2O–NaOAc); isomeric *diacetate*, m.p. 176—178° (Ac_2O–H_2SO_4); Me_1, m.p. 273° (decomp.) (Me_2SO_4–20% KOH), and Me_2 derivative (MeOH containing 3% HCl), m.p. 163—165°, sol. in N-NaOH but insol. in aq. $NaHCO_3$; two Me_3 derivatives (Et_2O–CH_2N_2) (*A*), m.p. 189—190°, (*B*) m.p. 126—128°, neither sol. in dil. NaOH; Br_1-derivative (Br in AcOH), m.p. 275°, and its Me_3 derivative, m.p. 175°]. (I) is decarboxylated by Cu chromite and quinoline at 220° in N_2 to a *compound*, m.p. 227—228°, which gives a blood-red ppt. with aq. $FeCl_3$ and a bright yellow solution in dil. NaOH. With KOH at 300° (I) yields 5 : 1 : 3-$OH{\cdot}C_6H_3(CO_2H)_2$ and a trace of $H_2C_2O_4$. Reduction (H_2, PtO_2, EtOH) of (I) gives some H_4-derivative [2 : 4-*dinitrophenylhydrazone*, m.p. 218—221° (decomp.)], whilst reduction with Zn and AcOH yields a compound, C_6H_8O (2 : 4-*dinitrophenylhydrazone*, m.p. 188—189°). Oxidation of (I) with O_3 and other oxidising agents causes deep-seated decomp.; (*A*) with Ag_2O in H_2O yields a little unidentified compound, m.p. 275° (decomp.). (I) may belong to the same class of compound as puberulic acid. *Me_2 5-methoxyisophthalate* has m.p. 109°. P. G. M.

Resynthesis of biotin from a degradation product. D. B. Melville, K. Hofmann, and V. du Vigneaud (*Science*, 1941, **94**, 308—309).—The diaminocarboxylic acid $C_9H_{18}O_2N_2S$ prepared from biotin (I) by the action of $Ba(OH)_2$ at 140° is reconverted into (I) by $COCl_2$. This provides further proof that (I) is a cyclic urea derivative. E. R. R.

ψ-Tanghinin, a new crystalline substance extracted from the kernels of *Tanghinia venenifera*. V. Hasenfratz (*Compt. rend.*, 1941, **213**, 404—406).—Treatment of the kernels with CS_2 removes ~58% of fatty matter from which tanghinin (I) (cf. A., 1889, 900; 1890, 171), m.p. 184°, $[\alpha]_D^{17}$ −69·7° in EtOH, is isolated. Treatment of the undissolved portion with boiling EtOH leads to the isolation of *ψ-tanghinin* (II), $C_{27}H_{40}O_8$, m.p. 248—250°, $[\alpha]_D^{25}$ −48·9° in EtOH. The colour reactions of (I) and (II) appear identical. (II) is converted by Ac_2O and NaOAc into a *diacetate*, m.p. 190°, $[\alpha]_D^{15}$ −82·6° in EtOH, also obtained from (I) and Ac_2O in presence of NaOAc or C_5H_5N; it appears that (I) is transformed into (II) before acetylation. H. W.

Osage orange pigments. IX. Improved separation; establishment of the *iso*propylidene group. M. L. Wolfrom and J. Mahan.

X. Oxidation. M. L. Wolfrom and S. M. Moffett (*J. Amer. Chem. Soc.*, 1942, **64**, 308—311, 311—315; cf. A., 1942, II, 179).—IX. Pptn. of pomiferin (**I**) by $Pb(OAc)_2$–MeOH–EtOH permits ready isolation of pure (**I**) (14·5) and osajin (**II**) (9·4 g.) from the fruit (1 kg. dry) of *Maclura pomifera*, Raf. With O_3 in AcOH, (**I**) and (**II**) give 0·7 mol. of $COMe_2$ and thus contain CMe_2:. Pomiferin Me_3 ether with KOH at 150° and later 300±10° gives $Bu^{\beta}CO_2H$ and *o*-$C_6H_4(OH)_2$; (**I**) yields similarly $H_2C_2O_4$. These products confirm the *iso*flavone structure.

X. Kuhn–Roth analysis of (**I**), (**II**), and 7 derivatives proves the presence of 2 CMe. With H_2O_2 in boiling KOH–$COMe_2$–H_2O, *osajetin* Me_3 (prep. by Me_2SO_4–KOH–H_2O–$COMe_2$ from the Me_2 ether), m.p. 75·5—76°, and Me_2 ether give anisic (**III**) and homoanisic acid, respectively. *Pomiferin* Me_4 (prep. as above), m.p. 64°, and Me_3 ether give similarly veratric (**IV**) and homoveratric acid. *Tetrahydro-osajetin* Me_3 *ether* (**V**) (prep. as above), m.p. 92°, and ScO_2 in boiling AcOH give *tetrahydro-osajetinone* Me_3 *ether* (**VI**), $C_{24}H_{25}O_3(OMe)_3$, m.p. 103—103·5°, which with boiling H_2O_2–KOH–$COMe_2$–H_2O gives (**III**) and *tetrahydro-osajylic acid* Me_2 *ether* (**VII**), $C_{16}H_{21}O(OMe)_2{\cdot}CO_2H$, m.p. 122—122·5°. With *iso*-$C_5H_{11}{\cdot}O{\cdot}NO$–NaOMe–MeOH at room temp. and later 0°, (**V**) gives the *oxime*, m.p. 163·5°, of (**VI**), converted into (**VI**) by $NaNO_2$ in aq. AcOH. *Tetrahydropomiferitin* Me_4 *ether* (prep. as above), m.p. 48·5—49°, gives similarly *tetrahydropomiferitinone* Me_4 *ether*, m.p. 82·5—83°, and thence (**IV**) and (**VII**). (**I**) and (**II**) thus have the same C-skeleton. R. S. C.

XI—ANALYSIS.

Simple weight-burette for use in organic analysis. P. Fantl (*Austral. J. Exp. Biol.*, 1941, **19**, 279—280).—The construction of a tap-less wt.-burette and its use for determining the equiv. wt. of sterol esters by the saponification method are described. J. N. A.

Quantitative drop analysis. XVI. Improved diffusion method for total nitrogen. E. R. Tomkins and P. L. Kirk (*J. Biol. Chem.*, 1942, **142**, 477—485).—A rapid procedure and apparatus are described whereby total N is determined with an accuracy ~0·3% on 1 μg. H. W.

Micro-analytical determination of chlorine and bromine in organic compounds with possible simultaneous determination of hydrogen. H. Gysel (*Helv. Chim. Acta*, 1941, **24**, 128—134E).—The substance is burnt in O_2 over a Pt contact and the products are passed through a dil. solution of KOH containing H_2O_2 ($Cl_2 + 2KOH + H_2O_2 = 2KCl + 2H_2O + O_2$). Cl is determined by addition of excess of $AgNO_3$ followed by back-titration with NH_4CNS until the first pink colour persistent for a few sec. is observed. With Br' this disappearance of colour is not observed. Since physical reasons compel the drying of the products of combustion previous to absorption of the halogen, it is possible to determine H simultaneously by use of a $CaCl_2$ tube. In presence of S the results for H are low owing to formation of H_2SO_4. The method is very suitable for serial analyses, 30—40 min. being required for halogen or 40—45 min. if H also is determined. H. W.

Micro-analytical method for determining methoxy- and ethoxy-groups in aromatic compounds. K. Bürger and F. Baláž (*Angew. Chem.*, 1941, **54**, 58—59).—After decomp. of the $AgNO_3$,AgI, the excess of $AgNO_3$ is titrated against 0·05N-KCNO, using $Fe^{III}NH_4$ alum as indicator. A. T. P.

Micro-method for identification of volatile liquids. Vapour pressure, b.p., and olefine content of *cyclo*butane and *cis*-Δ^{β}-butene. S. W. Benson (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 189—191).—An apparatus is described in which the v.p. of gases at various temp. is determined. In the determination of olefine content, the sample is dissolved in $CHCl_3$ and titrated with Br–AcOH at −10°. An accuracy of ~1% is obtained using *cyclo*pentene, *cyclo*heptene, C_4H_8, and C_5H_{10}. J. D. R.

Use of cobaltous sulphate in qualitative organic analysis. C. A. MacKenzie and K. C. Edson (*J. Chem. Educ.*, 1941, **18**, 332—333). —0·2 ml. (0·1 g. of solid) of the test solution is shaken with 3 ml. of 5% aq. $CoSO_4$. The formation of a blue ppt. of $Co(OH)_2$ within 5 min. differentiates the stronger from the weaker org. bases. The test is positive with piperidine, NEt_3, $NHBu^{\alpha}_2$, $NH_2{\cdot}[CH_2]_2{\cdot}OH$, $CH_2Ph{\cdot}NH_2$, 2 : 4 : 6-collidine, and α-picoline, and negative with NH_2Ph, C_5H_5N, α- and β-$C_{10}H_7{\cdot}NH_2$, etc. The effect of impurities on the test is discussed. The test can be used as a drop reaction. L. S. T.

Determination of methionine. E. F. Beach and D. M. Teague (*J. Biol. Chem.*, 1942, **142**, 277—284).—After hydrolysis by HI, methionine is pptd. as a thiolactone with Cu_2O, and the S determined as SO_4''. Results for 8 proteins are given. R. L. E.

Cystine tests of photographic importance. A. Steigmann (*J.S.C.I.*, **61**, 52).—Cystine (**I**) inhibits the reduction of ammoniacal $AgNO_3$ in presence of $(NH_4)_2SO_3$ but sensitises the reduction in presence of gelatin and traces of Fe" or cuprammonium salts. These two reactions used in conjunction are selective for detecting traces of (**I**). S. B.

Determination of copper reduced by sugars. Use of eeric sulphate as a volumetric reagent. A. H. Best, A. H. Peterson, and H. M. Sell (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 145—146).—The Cu_2O pptd. by the sugar is dissolved in $(NH_4)_2Fe(SO_4)_2$, and the Fe" produced is titrated at 50—60° with $Ce(SO_4)_2$ using *o*-phenanthroline–Fe" complex as indicator. The method gives the same results as the $KMnO_4$ method. J. D. R.

Fermentation of maltose and glucose in alkaline solution.—See A., 1942, III, 490.

Colorimetric determination of diethylstilbœstrol. M. Tubis and A. Bloom (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 309).—The diethylstilbœstrol in EtOH–H_2O is determined colorimetrically with a complex of phosphomolybdic–phosphotungstic acid. J. D. R.

Semimicrochemical assay for diethylstilbœstrol. C. W. Sondern and C. Burson [*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 358—359).—Bromination (6 mols.) of diethylstilbœstrol (**I**) yields (probably) βγδ-tribromo-γδ-di-(3 : 5-dibromo-4-hydroxyphenyl)hexane with elimination of 5 HBr. (**I**) with KBr–$KBrO_3$–HCl is kept at 30° for 30 min. and the excess of Br determined iodometrically. J. D. R.

Assay of benzaldehyde. Use of hydroxylammonium sulphate and aqueous sodium hydroxide. M. Schubert and J. G. Dinkelspiel (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 154—155).—The sample is added to a solution of NH_2OH,H_2SO_4 in MeOH (previously neutralised to tetrabromophenol-blue) and titrated with 0·1N-NaOH, using the same indicator and the same end-point. J. D. R.

Semi-micro qualitative test for 1 : 4-diketones. W. G. Leach (*Analyst*, 1942, **67**, 53).—The test solution is mixed with an excess of solid NH_4OAc and 2 drops of AcOH, boiled, and cooled. Excess of aq. H_2SO_4 is added, and a thin piece of bleached paper tissue consisting mainly of mechanical wood pulp and moistened with aq. HCl is immediately placed on the top of the test-tube. On boiling the solution, a pink stain appears on the paper if a 1 : 4-diketone is present. S. B.

Determination of hypoxanthine. G. H. Hitchings (*J. Biol. Chem.*, 1942, **143**, 43—48; cf. A., 1941, II, 276).—In the method described, hypoxanthine (≯1 mg. of N) is pptd. as Ag picrate, which is separated from AgCl (if present, *e.g.*, as a result of use of HCl to decompose Cu–purine complex) by dissolution in conc. HNO_3. The pptd. Ag is determined by titration with 0·01N-NH_4CNS after destruction of org. matter by digestion with $H_2SO_4 + HNO_3$. A blank determination is also made. Guanine and adenine interfere and must first be removed. Interference by xanthine occurs only if its concn. is high and is wholly or partly counteracted by increasing the concn. of HNO_3. The error is ~1% and is not greatly increased when the amount of hypoxanthine-N is 0·5 mg. W. McC.

Determination of allantoin by the Rimini–Schryver reaction.—See A., 1942, III, 503.

Analysis of hexamethylenetetramine. I. Composition and properties of additive products of hexamethylenetetramine with hydrochloric acid and calcium chloride. Y. Oohara (*J. Soc. Rubber Ind. Japan*, 1936, **9**, 419—431).—Additive compounds of $(CH_2)_6N_4$ with $CaCl_2$ and HCl can be pptd. with C_6H_6. The $CaCl_2$ compound gives a coloration with Co oleate. Ch. Abs. (*w*)

Determination of methenamine [hexamethylenetetramine]. E. F. Slowick and R. S. Kelley (*J. Amer. Pharm. Assoc.*, 1942, **31**, 15—19).—The U.S.P. XI method is slow and inaccurate; slight modifications to improve the accuracy are suggested. Pptn. methods and methods in which H_2O_2, $KBrO_3$, or alkaline NaOCl is used as oxidising agent are unsatisfactory. Oxidation by $Ca(OCl)_2$ affords an accurate and rapid method. F. O. H.

Determination of pyramidone. J. de D. Guevara (*Bol. Soc. Quim. Peru*, 1941, **7**, 221).—A solution of pyramidone (**I**) in H_2SO_4 is made alkaline with aq. NaOH or NH_3 and extracted with $CHCl_3$. The H_2O-washed extract is filtered through cotton into a tared vessel, the residue after drying at 100° being taken as (**I**). (**I**) may also be determined by treatment with picric acid and titration of the excess with NaOH. F. R. G.

Determination of quinine and assay of quinine and strychnine in mixtures. R. L. Herd (*J. Amer. Pharm. Assoc.*, 1942, **31**, 9—11).—Quinine (**I**) may be determined by titration with 0·01N-$HClO_4$ in glacial AcOH, using α-naphtholbenzein as indicator (cf. Nadeau and Branchen, A., 1936, 353). A method for the separation and determination of (**I**) and strychnine (**II**), based on the extraction of (**II**) by a solution of $CHCl_2{\cdot}CO_2H$ in $CHCl_3$, is described. F. O. H.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

AUGUST, 1942.

I.—ALIPHATIC.

New methods of preparative organic chemistry. XIII. Hydrogenations with Raney catalysts. R. Schröter. **XIV. Boron fluoride as catalyst in chemical reactions.** D. Kästner (*Angew. Chem.*, 1941, **54**, 252—260, 296—304). H. W.

Reactive paraffins. (A) E. E. Gilbert. (B) H. C. Brown and M. S. Kharasch (*J. Chem. Educ.*, 1941, **18**, 435—438, 589).—The reactivity of the paraffin hydrocarbons is illustrated by a review of thermal conversions, alkylations, oxidations, halogenations, and nitrations. L. S. T.

Oxidation of hydrocarbons at low temperatures. P. George, E. K. Rideal, and A. Robertson (*Nature*, 1942, **149**, 601—602).—Results of experiments on the uncatalysed and heavy-metal-catalysed oxidation of alkylbenzene and long-chain saturated aliphatic hydrocarbons (C_{15-25}) in the liquid phase at 100—120° support the hypothesis that hydroperoxides (**I**) are primary oxidation intermediates, peroxide yields representing respectively 60—80 and 5% of the O_2 absorbed. The metallic catalyst both starts and stops reaction chains leading to the production of (**I**) and decomposes them, catalysts showing marked specificity. The long-chain alkyl (**I**) decompose almost exclusively to give ketones. A. A. E.

Products of the joint action of sulphur dioxide and chlorine on aliphatic hydrocarbons in ultra-violet light. I. Propane in carbon tetrachloride. F. Asinger, W. Schmidt, and F. Ebeneder. **II. *n*-Butane in carbon tetrachloride.** F. Asinger, F. Ebeneder, and E. Böck (*Ber.*, 1942, **75**, [*B*], 34—41, 42—48).—I. Simultaneous passage of C_3H_8, Cl_2, and SO_2 (2·5 : 1·1 : 1 vol.) into CCl_4 in ultra-violet light at room temp. gives a mixture of equal parts of propane-α- and -β-monosulphonyl chlorides, chloro- and dichloro-propanemonosulphonyl chlorides, with a small amount of more highly chlorinated products of C_3H_8; the non-volatile residue contains $CH_2(CH_2{\cdot}SO_2Cl)_2$, m.p. 48°. The following appear new: *propane-αγ-disulphonamide*, m.p. 173°, and *-disulphonanilide*, m.p. 130°; *α-thiocyanopropane*; *propane-α-sulphonanilide*, a liquid; *propane-β-sulphonamide*, m.p. 65·7°, and *-sulphonanilide*, m.p. 84°.

II. Exposure of a mixture of C_4H_{10}, Cl_2, and SO_2 (2·5 : 1 : 1·1 vol.) to ultra-violet light gives mono-, di-, and chloro-sulphonyl chlorides in the ratio 85 : 10—11 : 3—5 or in the ratio 10 : 85—90 : 3—5 when the vol. ratio is 0·55 : 1 : 1·1. The following appear new: *butane-αδ-disulphonyl chloride*, m.p. 83·5° (corresponding *disulphonamide*, m.p. 182°, and *disulphonanilide*, m.p. 188·5°); *butane-αγ-disulphonyl chloride*, m.p. 41°, and *-disulphonanilide*, m.p. 170°; *butane-α-sulphonyl chloride*, b.p. 93·5°/15 mm., and *-sulphon*cyclo*hexylamide*, m.p. 71·8°; *butane-β-sulphonyl chloride*, b.p. 85°/15 mm., and *-sulphon*cyclo*hexylamide*, m.p. 58°; *αδ-dithiocyanobutane*, a liquid; *butane-αγ-disulphonyl chloride*, m.p. 41°, and *-disulphonanilide*, m.p. 170°; *αγ-dithiocyanobutane*. H. W.

Polymerisation of ethylene and propylene by free alkyl radicals.—See A., 1942, I, 270.

Mechanism of propylene and propane formation during electrolysis of butyric acids.—See A., 1942, I, 273.

Catalytic oxidation of acetylene.—See A., 1942, I, 271.

Acetylenic analogue of neopentyl bromide. Evidence that the hindrance to displacement reactions in neopentyl halides is steric in nature. P. D. Bartlett and L. J. Rosen (*J. Amer. Chem. Soc.*, 1942, **64**, 543—546).—CMeBu$^{\gamma}$Cl$_2$ [obtained with much CH$_2$:CBu$^{\gamma}$Cl (**I**), b.p. 97—99°, from COMeBu$^{\gamma}$ by PCl_5 at 0—5°], b.p. 151—152°, gives CH$_2$:CBu$^{\gamma}$, b.p. 36·4—37·8°/768·3 mm. [also obtained in 80·5% yield from (**I**) by KOH–EtOH at 160—165°], which with MgEtBr–Et$_2$O and then dry CH_2O gives *δδ-dimethyl-Δ$^{\beta}$-pentin-α-ol* (**II**) (70·5%), b.p. 71·6°/18 mm., 162·4—163·4°/767·6 mm. (*p-bromo-*, m.p. 63—64·5°, and 3 : 5-*dinitro-benzoate*, m.p. 101·5—102°; *α-naphthyl-*, m.p. 163—164°, and *phenyl-urethane*, m.p. 81·5—82·5°), converted by PBr$_3$–C_5H_5N–Et$_2$O into *δδ-dimethyl-Δ$^{\beta}$-n-pentinyl bromide* (**III**) (41%), b.p. 50—52·5°/18—20 mm. Hydrogenation (PtO$_2$) of (**II**) in EtOH gives Bu$^{\gamma}$·[CH$_2$]$_3$·OH, b.p. 74°/22 mm. (α-naphthyl-, m.p. 80—81°, and *phenyl-urethane*, m.p. 51—52°; 3 : 5-*dinitrobenzoate*, m.p. 66—67°), which with PBr$_3$–Et$_2$O gives the bromide (**IV**), b.p. 61·5—62°/31 mm. Relative *k* (bimol.) for interaction of the bromides with KI in COMe$_2$ at 25±0·05° are Bu$^{\alpha}$ 465—474, *n*-C_7H_{15} 543—570, CH$_2$Bu$^{\gamma}$ 1, CHMeEt·CH$_2$ 29, Bu$^{\gamma}$·[CH$_2$]$_2$ 19—20, (**IV**) 470, allyl 30,300—33,200, CBu$^{\alpha}$:C·CH$_2$ 17,700—18,300, and (**III**) 22,300—23,300. The low reactivity of CH$_2$Bu$^{\gamma}$Br is thus due to steric causes (indicated by Stuart models) since the effect is not transmitted through unsaturated linkings. R. S. C.

Reaction of halogens and magnesium with alcohols and esters. V. Reaction of iodine and magnesium with alcohols. M. T. Dangjan (*J. Gen. Chem. Russ.*, 1941, **11**, 616—618).—I and Mg react with MeOH, EtOH, Bu$^{\alpha}$OH, and *iso*-C_5H_{11}·OH giving the respective alkyl iodides (yields 54·5, 61·2, 80·3, and 60·3%). The poor yields of the first two iodides are due to side reactions, that of the last to decomp. of the final product. G. A. R. K.

Essential oils. II. Occurrence of Δ$^{\gamma}$-hexen-α-ol in natural raspberry oil. H. Bohnsack (*Ber.*, 1942, **75**, [*B*], 72—74).—The oil obtained by extraction of the expressed juice with Et$_2$O, removal of the latter, and distillation of the residue with steam contains EtOH, Bu$^{\beta}$OH, *iso*-C_5H_{10}·OH, and Δ$^{\gamma}$-hexen-α-ol, b.p. 65—67°/15 mm. (α-naphthylurethane, m.p. 69—70°; *formate*, b.p. 53—55°/12 mm.; *acetate*, b.p. 66°/16 mm.; iso*butyrate*, b.p. ~80°/14 mm.), oxidised to $H_2C_2O_4$ and EtCO$_2$H and hydrogenated (PtO$_2$ in AcOH) to *n*-hexanol (α-naphthylurethane, m.p. 60—61°). H. W.

Decomposition of acetylenic carbinols. A. F. Thompson, jun., and C. Margnetti (*J. Amer. Chem. Soc.*, 1942, **64**, 573—576).—By passage over hot, commercial (*i.e.*, alkaline) Al_2O_3, CR:C·CR′(CH$_2$R″)·OH are smoothly dehydrated to CR:C·CR′:CHR″, unless R = H, Ph, or Me in which cases 50—100% of cleavage to CR:CH + COR′·CH$_2$R″ occurs (cf. Thompson *et al.*, A., 1941, II, 83). The nature of R′ and R″ has little effect. 50—66% aq. KOH effects only the latter decomp., lower concns. being without action; solid KOH or KOH–EtOH causes the decomp. but the ketone formed reacts further. Condensation of CORR′ with CR″:C·MgX in Et$_2$O gives *γ-methyl-Δ$^{\delta}$-n-hexin-γ-ol*, m.p. 132—135°, *γζ-di-*, b.p. 128—130°/35 mm., and *γζζ-tri-methyl-Δ$^{\delta}$-n-hexin-γ-ol*, b.p. 137—140°/35 mm., *ε-phenyl-γ-methyl-Δ$^{\delta}$-n-pentin-γ-ol*, b.p. 138—140°/15 mm., *δ-methyl-Δ$^{\beta}$-n-nonin-δ-ol*, b.p. 105—108°/15 mm., *α-phenyl-γ-methyl-Δ$^{\alpha}$-n-octin-γ-ol*, b.p. 114—117°/2 mm., *β-methyl-γ-*iso*propyl-Δ$^{\delta}$-n-nonin-γ-ol*, b.p. 130—133°/15 mm., (?) *γζ-dimethyl-Δ$^{\beta}$-n-octen-Δ$^{\delta}$-in-ζ-ol*, b.p. 117—120°/15 mm., and (?) *γζ-dimethyl-Δ$^{\beta}$-n-undecen-Δ$^{\delta}$-in-ζ-ol*, b.p. 115—118°/5 mm. Pr$^{\alpha}$CO$_2$Et with CBu$^{\alpha}$:C·MgX gives *η-n-propyl-Δ$^{\epsilon 0}$-tridecadi-in-η-ol*, b.p. 130—132°/2 mm., which over Al_2O_3 gives CHEt:C(C:CBu$^{\alpha}$)$_2$; *η-phenyl-Δ$^{\epsilon 0}$-tridecadi-in-η-ol*, b.p. 168—170°/2 mm. (similarly prepared from EtOBz), over Al_2O_3 gives CBu$^{\alpha}$:CH and a resin (formed from CBu$^{\alpha}$:C·COPh). R. S. C.

Structure and properties of [dehydration and dehydrogenation] catalysts.—See A., 1942, I, 272.

Mechanism of dehydration and dehydrogenation of alcohols of the homologous series C_nH_{2n+1}·OH on homogeneous catalysts.—See A., 1942, I, 272.

Alkyl carbonates. III. Condensation with nitriles. Synthesis of α-cyano-esters. V. H. Wallingford, D. M. Jones, and A. H. Homeyer. **IV. Alkylation of malonic esters by alkyl carbonates.** V. H. Wallingford and D. M. Jones. **V. Alkyl carbonates as solvents for metalation and alkylation reactions.** V. H. Wallingford, M. A. Thorpe, and A. H. Homeyer (*J. Amer. Chem. Soc.*, 1942, **64**, 576—578, 578—580, 580—582; cf. A., 1941, II, 349).—III. CN·CHR·CO$_2$R′ are obtained in good yield by boiling CH$_2$R·CN, R′$_2$CO$_3$, and NaOEt with continuous removal of EtOH. KOEt, but not Mg(OEt)$_2$ or Al(OEt)$_3$, may be used. Yields increase as R′ increases in mol. wt., *i.e.*, as the b.p. rises. CHPhEt·CN does not react and no reaction occurs if R is *sec.* CH$_2$:CH·CH$_2$·CN and *p*-NO$_2$·C$_6$H$_4$·CH$_2$·CN are too reactive and give tars. *Et α-cyano-phenyl-*, b.p. 125—126°/2—3 mm. (amide, m.p. 148—149°), -*p-iodo-phenyl-*, b.p. 160°/2 mm., and -*p-tolyl-acetate*, b.p. 120—121°/1 mm., are described.

IV. CRNa(CO$_2$R′)$_2$ [prepared from CHR(CO$_2$R′)$_2$ and NaOR″ by removing R″OH by distillation] in boiling R′$_2$CO$_3$ at, usually, 125—175° gives CRR′(CO$_2$R′)$_2$ in yields stated below. In general R should = R″, but for prep. of (**I**) (below) NaOMe can be used. Yields are good if R′ is primary, independently of the mol. wt., but

poor if R′ is *sec.* $CHNa(CO_2R')_2$ cannot be used as it gives $CH(CO_2R')_3$. The K derivatives can be used and, for $CHEt(CO_2Et)_2$, $Mg(OEt)_2$ at 225°. $CH_2R{\cdot}CO_2R'$ can also be used as starting material, since with NaOR′ and R'_2CO_3 it gives $CRNa(CO_2R')_2$. The following are thus prepared: $CEtR(CO_2Et)_2$ in which R = Et [from $Pr^{\alpha}CO_2Et$ 36%; from $CHEt(CO_2Et)_2$ 54%], Bu^{α} (from $C_5H_{11}{\cdot}CO_2Et$ 34%), *iso*amyl (from $Pr^{\beta}{\cdot}[CH_2]_3{\cdot}CO_2Et$ 45%), Pr^{β} (from $Bu^{\beta}CO_2Et$ 10%), octyl (25%), CHMeEt (poor), and Ph (30%), m.p. −9° to −7°, b.p. 105°/1 mm.; *Bu*$^{\alpha}_2$ *ethylbutyl-* (42%), b.p. 117—119°/1 mm., *butyl*-n-*hexadecyl-* (83%), b.p. 265—268°/4 mm., and *benzylbutyl-malonate* (80%), b.p. 172°/3 mm. (derived *acid*, m.p. 105—107°); *Bu*$^{\beta}_2$ *ethyliso*butylmalonate (45%), b.p. 175°/30 mm. (derived *acid*, m.p. 109—110°); *di*isoamyl *ethyliso*amylmalonate (60%), b.p. 126—129°/1 mm. (derived *acid*, m.p. 120—121°); $(CHMeEt)_2C(CO_2CHMeEt)_2$ (poor yield); impure *di-γ-pentyl ethyl-γ-pentylmalonate* (~20%), b.p. 132—134°/3 mm.; $(CH_2Ph)_2$ *benzylethylmalonate* (53%), b.p. 245—247°/2 mm. (derived *acid*, m.p. 125—127°). Fluorene gives 45% of *Bu* 9-*butylfluorene*-9-*carboxylate*, b.p. 175—176°/2 mm. (derived *acid*, m.p. 112—114°). The following are incidentally described: *Bu*$^{\alpha}_2$ *ethyl-*, b.p. 98—99°/2 mm., n-*hexadecyl-*, b.p. 255—260°/4—5 mm., and *benzyl-malonate*, b.p. 154°/1 mm.; *Bu*$^{\beta}_2$, b.p. 150°/28 mm., *di*isoamyl, b.p. 96°/1 mm., *di-γ-pentyl*, b.p. 168—169°/35 mm., and $(CH_2Ph)_2$ *ethylmalonate*, b.p. 190°/2 mm.; $(CHMeEt)_2$ sec.-*butylmalonate*, b.p. 115°/3 mm.

V. Alkylations of malonic, acetoacetic, β-keto- and α-cyano-acetic esters are well effected by alkyl halides and NaOEt [or KOEt or, in one case, $Mg(OEt)_2$] in boiling Et_2CO_3, when the EtOH formed is removed. Di-*sec.*-alkylmalonates can thus be prepared. During some difficult alkylations exchange of ester groups occurs but may be avoided by suitable choice of alkyl groups. The limiting factor is probably elimination of HHal from the alkyl halide; this is noteworthy with $Bu^{\beta}Br$ and prohibitive with $Bu^{\gamma}Cl$ or $Bu^{\gamma}Br$ which give solely $CMe_2{:}CH_2$ without alkylation. The following are described: *Et*$_2$ n-*butyliso*amyl-, b.p. 91—93°/1·5 mm., n-*butyl*-sec.-*butyl-*, b.p. 114—116°/4·5 mm., sec.-*butyliso*amyl-, b.p. 95—99°/2—2·5 mm., *allyl*-sec.-*butyl-*, b.p. 109—111°/5 mm., sec.-*butyl*-n-*amyl-*, b.p. 89·5—92·5°/1—1·5 mm., *di*-sec.-*butyl-*, b.p. 112—114°/1·5 mm., *allyl*-tert.-*butyl-*, b.p. 94—95·5°/3·5 mm., iso*propyl*-iso-, b.p. 119—121°/10 mm., and -sec.-*butyl-*, b.p. 120—123°/10 mm., n-*propyl*-n-*amyl-*, b.p. 99—101°/2·6 mm., and *benzyl*-n-*hexadecyl-*, b.p. 238—240°/1 mm., *-malonate*; *Bu*$^{\alpha}$ α-*benzoyl*-n-*butyrate*, b.p. 116—117°/1 mm.; *Pr*$^{\alpha}$ α-*cyano*-α-*ethyl*-iso*hexoate*, b.p. 64—67°/1 mm., and β-*keto*-α-*ethyl*-n-*nonoate*, b.p. 103—105°/3·5 mm.; *Et* α-*cyano*-α-p-*tolyl*-n-*butyrate*, b.p. 105—110°/2·5—3 mm.; α-*benzyl*-n-*octadeco*-2 : 4 : 6-*tribromoanilide*, m.p. 85—87°. R. S. C.

Thioglycerol and related compounds of sulphur. B. Sjöberg (*Ber.*, 1942, **75**, [*B*], 13—29).—α-*Monothioglycerol* [*βγ-dihydroxy-α-thiolpropane*] (**I**), b.p. 95°/9 mm., 112°/3 mm., is obtained by treating γ-hydroxypropylene αβ-oxide (**II**) with $Ba(OH)_2$ and H_2S or from (**II**) and AcSH, whereby the primary product is a mixture of *βγ-dihydroxy-α-acetylthiolpropane*, b.p. 125—135°/1·8 mm., and the β- or γ-monoacetate; this is hydrolysed (HCl–MeOH at 60°) to (**I**). Alternatively, $CH_2Br{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, obtained from $OH{\cdot}CH(CH_2{\cdot}OH)_2$ and HBr and purified through the CMe_2 derivative, is converted by AcCl into the *diacetate*, b.p. 88—90°/1 mm., transformed by AcSK into the *diacetate thioacetate*, b.p. 130—136°/1·8 mm., which is hydrolysed to (**I**). α-Chloro-*βγ-iso*propylidenedioxypropane and aq. KSH at 100° yield *βγ-iso*propylidenedioxy-α-*thiolpropane* (**II**), b.p. 54—57°/5 mm., and the corresponding *αα′-disulphide*, b.p. 145—153°/3·5 mm. Condensation (P_2O_5–sand) of (**I**) with $COMe_2$ at 0° affords (**II**) and α-*hydroxy-βγ-iso*propylidene*oxythiopropane*, b.p. 58—60°/0·8 mm., which appears to re-form (**II**) to some extent when kept. $CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}OH$ and NaSH yield *γ-hydroxy-αβ-dithiolpropane* (**III**), b.p. 91·5—92°/1·7 mm., also obtained by means of KSAc. *αβ′-Dibromohydrin γ-acetate*, b.p. 51°/0·3 mm., and KSAc give *γ-acetoxy-αβ-diacetylthiolpropane*, b.p. 125—130°/0·6 mm., hydrolysed (HCl–MeOH) to (**III**). $OH{\cdot}CH(CH_2Cl)_2$ and NaSH in abs. EtOH yield $OH{\cdot}CH(CH_2{\cdot}SH)_2$, b.p. 82°/1·5 mm., purified through the Hg derivative, which softens and blackens at 190—190·5°. $Cl{\cdot}[CH_2]_3{\cdot}OH$ and K_2S_2 in H_2O afford *γγ′-dihydroxydipropyl disulphide*, b.p. 160°/0·8 mm., reduced at a Pb cathode to $OH{\cdot}[CH_2]_3{\cdot}SH$ (**IV**), b.p. 80°/1·2 mm. Propylene αβ-oxide and AcSH at 60—70° give mainly *β-hydroxy-α-acetylthiolpropane*, b.p. 80—100°/12 mm., hydrolysed (HCl–MeOH) to *β-hydroxypropylthiol* (**V**), b.p. 51°/12 mm. (**IV**) and (**V**) afford CPr_2 derivatives, b.p. 60°/12 mm. and 72°/80 mm., or 141°/761 mm., respectively. (**V**) is transformed by conc. HCl at 100° into *β-chloropropylthiol*, b.p. 125—125·5°/764 mm., which immediately decomposes in H_2O at 0°. H. W.

Characterisation of lactic acid as the benziminazole derivative. R. J. Dimler and K. P. Link (*J. Biol. Chem.*, 1942, **143**, 557—558).—*d-* or *l-*, m.p. 165—177° (hydrochloride, m.p. 213—215°), and *dl-*lactobenziminazole, m.p. 179—181° (hydrochloride, m.p. 211—213°), are prepared. A. T. P.

Acid synthesis. II. Effect of hindrance. Methyl-*tert.*-butyl- and -ethylpropyl-acetic acids. J. G. Aston, J. T. Clarke, K. A. Burgess, and R. B. Greenburg (*J. Amer. Chem. Soc.*, 1942, **64**, 300—302; cf. A., 1941, II, 4).—Conversion of $COR{\cdot}CR'R''Br$ by $NaOR'''$ into $CRR'R''{\cdot}CO_2R'''$ occurs owing to steric hindrance around the Br and is retarded if R is large. $COMe{\cdot}CHMeBr$ and NaOMe in boiling Et_2O give, by normal metathesis, *γ-methoxybutan-β-one* (39·1%), b.p. 87°/740 mm. [with $NHPh{\cdot}NH_2$ in 5% HCl gives $(CMe{:}N{\cdot}NHPh)_2$]. *γ-Bromo-δδ-dimethylpentan-β-one* (prep. from $COMe{\cdot}CH_2Bu^{\gamma}$ by Br at 0°), b.p. 106°/88 mm., and NaOMe–Et_2O give *Me αββ-trimethyl*-n-*butyrate* (73%), b.p. 95°/150 mm. [derived *acid*, m.p. 53·5°, b.p. 132°/55 mm.; anilide, m.p. 112°)]. $COPr^{\alpha}{\cdot}CHMeEt$ and Br at 0° give *γ-bromo-γ-methyl*-n-*heptan-δ-one* (45%), b.p. 88°/22 mm., which with NaOMe–Et_2O gives a const.-boiling mixture (75%) of $COPr^{\alpha}{\cdot}CMeEt{\cdot}OMe$ (gives a small amount of 2 : 4-dinitrophenylhydrazone, m.p. 139—140°) and $CMeEtPr^{\alpha}{\cdot}CO_2Me$, whence boiling HI yields *α-methyl-α-ethyl*-n-*valeric acid*, b.p. 105°/20 mm. (*chloride*, b.p. ~110°/100 mm.). $COPh{\cdot}CMe_2Br$ and NaOMe–Et_2O give 70% of α-methoxy*iso*butyrophenone, b.p. 88—88·5°/14 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 139—140°), oxidised by $K_2Cr_2O_7$–H_2SO_4 at 75—80° to $COMe_2$ and BzOH. R. S. C.

Second *dl*-βζ-epoxy-Δ$^{\gamma}$-heptene-γ-carboxylic acid. M. Delépine and M. Badoche (*Compt. rend.*, 1941, **213**, 413—416).—Oxidation with $Ba(OH)_2$ and $AgNO_3$ of the dimeride of $CHMe{:}CH{\cdot}CHO$ gives 1% of *dl-βζ-epoxy-Δ$^{\gamma}$-heptene-γ-carboxylic acid*-b, m.p. 93—93·5° [*bromohydrin* (+H_2O), m.p. 101—106° (slight decomp.); *amide*, m.p. 168° (slow heating)], hydrogenated (Ni) to the H_2-acid [*anilide*, m.p. 168—169° (slow heating)]. A. Li.

Complex formation by ascorbic acid with formaldehyde.—See A., 1942, III, 407.

Colour reaction of dehydroascorbic acid. J. H. Roe and C. A. Kuether (*Science*, 1942, **95**, 77).—The red colour formed by the action of H_2SO_4 and the coupled 2 : 4-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$–dehydroascorbic acid compound is suitable for the colorimetric determination of ascorbic acid. High concns. of pentoses, glucose, and fructose may interfere. E. R. R.

Carbohydrate characterisation. III. Identification of hexuronic or saccharic acids as benziminazole derivatives. R. Lohmar, R. J. Dimler, S. Moore, and K. P. Link (*J. Biol. Chem.*, 1942, **143**, 551—556; cf. A., 1940, II, 244).—A method for identifying naturally occurring hexuronic acids as dibenziminazole derivatives of the corresponding saccharic acids is described. Thus, *d*-glucuronic, *d*-mannuronic, and *d*-galacturonic acid are oxidised to the respective dibasic acid, which with *o*-$C_6H_4(NH_2)_2$–HCl–H_3PO_4–$(OH{\cdot}[CH_2]_2)_2O$ at ~135° afford d-*saccharo-*, m.p. 238°, $[\alpha]_D^{25}$ +60·3° in aq. citric acid [*dihydrochloride*, m.p. 257—258° (decomp.); *picrate*, m.p. 211° (decomp.)], d-*mannosaccharo-*, m.p. 250°, $[\alpha]_D^{25}$ −1·3° in H_2O [*dihydrochloride*, m.p. 256—257° (decomp.); *picrate*, m.p. 241° (decomp.); *tetra-acetate*, m.p. 255—256°, $[\alpha]_D^{25}$ −11·9° in $CHCl_3$], and *mucic acid-dibenziminazole*, m.p. 298°, $[\alpha]_D^{25}$ 0·0° in aq. citric acid [*dihydrochloride*, m.p. 318° (decomp.); *picrate*, m.p. 250° (decomp.)], respectively. A. T. P.

Photochemical reaction between bromine and choral.—See A., 1942, I, 273.

Dimeric *dl*-glyceraldehyde αγ-diphosphate. E. Baer and H. O. L. Fischer (*J. Biol. Chem.*, 1942, **143**, 563—564).—Dimeric *dl*-glyceraldehyde and $(OPh)_2POCl$–C_5H_5N give, after hydrogenation (PtO_2–MeOH at room temp.) of the resulting Ph_8 ester, m.p. 108—109°, dimeric *glyceraldehyde αγ-diphosphate* [*Ba*′ (+$2H_2O$) and *Ca* (+$2H_2O$) salt], which is probably an intermediate in sugar metabolism. A. T. P.

Reaction of keten diethyl acetal with αβ-unsaturated carbonyl compounds.—See A., 1942, II, 227.

Intramolecular condensations in polymerides. F. T. Wall (*J. Amer. Chem. Soc.*, 1942, **64**, 269—273).—Mathematical. The fractions of O remaining in infinitely long "head to tail," random, and "head to head–tail to tail" polymerides after complete intramol. aldol condensations have been calc. statistically. The results for pure polymerides (*e.g.*, of $COMe{\cdot}CH{:}CH_2$) have been extended to co-polymerides. W. R. A.

Action of sodium on hexamethylacetone. P. G. Stevens and J. H. Mowat (*J. Amer. Chem. Soc.*, 1942, **64**, 554—556).—Results recorded below differ from those of Favorsky *et al.* (A., 1934, 758), possibly for steric reasons. With Na–Et_2O–N_2 at > room temp. $COBu^{\gamma}_2$ gives $CHBu^{\gamma}_2{\cdot}OH$ and 5% of *ββεε-tetramethyl-γδ-di-*tert.-*butyl*-n-*hexane-γδ-diol* (**I**), m.p. 116—117°, b.p. ~200°/13 mm., and a mixture (C 77·2, H 13·6%), b.p. 125—126°/14 mm., 68°/0·8 mm. (*tetrabromide*, m.p. 75—78·5°). (**I**) is stable to $Pb(OAc)_4$–C_6H_6 at 25° and 100° and to boiling $KMnO_4$–C_5H_5N, contains 2 active H, has normal mol. wt. in camphor and *cyclo*hexane but not in C_6H_6 at 5°, does not absorb O_2 or give free radicals, and in conc. H_2SO_4 at −20° (later 25°) gives an unsaturated (Br; $KMnO_4$) oil, b.p. 41—120°/25 mm. (no insol. bromide). R. S. C.

Application of 2-nitroindane-1 : 3-dione to the isolation and identification of organic bases. G. Wanag and A. Dombrowski (*Ber.*, 1942, **75**, [*B*], 82—86; cf. A., 1937, II, 199).—2-Nitroindane-1 : 3-dione (**I**) (modified prep. described) in ~5·7% solution in H_2O gives non-hygroscopic, anhyd. ppts. with the following: NH_2Me, m.p. 203—205°; NH_2Et, m.p. 202—203°; NH_2Pr^{α}, m.p. 184—185°;

NH_2Pr^{β}, m.p. 205°; NH_2Bu^{α}, m.p. 147°; NH_2Bu^{β}, m.p. 178°; n-$C_5H_{11}\cdot NH_2$, m.p. 158°; iso-$C_5H_{11}\cdot NH_2$, m.p. 162°; iso-$C_6H_{13}\cdot NH_2$, m.p. 155°; n-$C_7H_{15}\cdot NH_2$, m.p. 149—150°; $CH_2Ph\cdot CHMe\cdot NH_2$, m.p. 193°; *cyclo*hexylamine, m.p. 213°; $CH_2(NH_2)_2$ (1 : 2), m.p. 229°; $(CH_2\cdot NH_2)_2$ (1 : 2), m.p. 204—205°; *propylenediamine* (1 : 2), m.p. 206°; *diaminopropanol*, m.p. 195°; $NHBu^{\beta}\cdot CH_2Ph$, m.p. 220°; *mesidine*, m.p. 162°; *ψ*-cumidine, m.p. 162°; s-m-*toluylenediamine*, m.p. 166°; 1 : 2-, m.p. 179°, and 1 : 8-$C_{10}H_6(NH_2)_2$ (1 : 2), m.p. 216°; *naphthidine*, m.p. 195°; 1-$C_{10}H_7\cdot NHMe$, m.p. 196—199°; 2-$C_{10}H_7\cdot NHMe$, m.p. 177°; o-, m.p. 182°, m-, m.p. 192°, and p-, m.p. 188°, $\cdot C_6H_4Cl\cdot NH_2$; o-, m.p. 203—205°, and m-, m.p. 210°, $\cdot NH_2\cdot C_6H_4\cdot OH$; o-, m.p. 198°, m-, m.p. 205°, and p-, m.p. 203°, $\cdot NH_2\cdot C_6H_4\cdot OMe$; o-, m.p. 206°, m-, m.p. 210°, and p-, m.p. 190°, $\cdot NH_2\cdot C_6H_4\cdot OEt$; *o-dianisidine*, m.p. 226°; 2 : 4 : 1-$(NH_2)_2C_6H_3\cdot OH$, (1 : 2), m.p. 198—200°; p-$C_6H_4Ac\cdot NH_2$, m.p. 199°; p-$NH_2\cdot C_6H_4\cdot SO_2\cdot NH_2$, m.p. 214°; m-, m.p. 182°, and p-, m.p. 175°, $\cdot NO_2\cdot C_6H_4\cdot NH_2$; o-, m.p. 189°, m-, m.p. 212°, and p-, m.p. 213°, $\cdot NH_2\cdot C_6H_4\cdot CO_2H$; o-$NH_2\cdot C_6H_4\cdot CO_2Et$, m.p. 197°; 4-*methylquinoline*, m.p. 197—198°; iso*quinoline*, m.p. 187°; 2 : 6-*diaminopyridine* (1 : 2), m.p. 235°; 2-*aminothiazole*, m.p. 208°; *pyrrolidine*, m.p. 215°; *aziminobenzene*, m.p. 178°; *benziminazole*, m.p. 228°. Except where otherwise stated the ratio base : (**I**) = 1 : 1. Limiting concns. are recorded at which (**I**) gives ppts. with the above mentioned bases and also with putrescine, cadaverine, histamine, mescaline, $COPh\cdot CH_2\cdot NH_2$, spermine, 1 : 3 : 5-$C_6H_3(NH_2)_3$, 1 : 2 : 4 : 6-$C_6H_2Me(NH_2)_3$, 1 : 2 : 4 : 6-$C_6H_2Cl(NH_2)_3$, tetra-aminoditolylmethane, 1 : 4-, 1 : 5-, and 2 : 7-$C_{10}H_6(NH_2)_2$, o-$C_6H_4(NHMe)_2$, o-$NHAc\cdot C_6H_4\cdot NH_2$, o-$C_6H_4(CO)_2N\cdot C_6H_4\cdot NH_2$-*o*, p-$NH_2\cdot C_6H_4\cdot N_2Ph$, chrysoidine, methylene- and ethylene-dianiline, piperazine, nitron, narcotine, 3 : 5-dimethylpyrazole, and $NHPh\cdot NH_2$. H. W.

Ethanolamine 3 : 5-di-iodosalicylate, m.p. 199—200° (corr.; decomp.).—See A., 1942, III, 463.

Chromatographic separation of mixtures of amino-acids. J. Wachtel and H. G. Cassidy (*Science*, 1942, **95**, 233; cf. A., 1942, II, 44).—Quant. separations of mixtures of *l*-tyrosine (**I**) and *dl*-leucine (**II**), of *dl*-phenylalanine (**III**) and (**II**), and partial separations of mixtures of (**I**) and (**III**) and of glycine and phenylalanine, are effected by a modified Tswett chromatographic method in which the adsorbent is a commercial C (Darco G-60) mixed with filter pulp. E. R. R.

Preparation of glycine. W. C. Tobie and G. B. Ayres (*J. Amer. Chem. Soc.*, 1942, **64**, 725).—Prep. of glycine (Orten *et al.*, A., 1931, 1042) is improved to give 80% yield. R. S. C.

Complex calcium and copper salts of trilon *A* and *B*. P. Pfeiffer and W. Offermann (*Ber.*, 1942, **75**, [*B*], 1—12).—$NH(CH_2\cdot CO_2Na)_2,6H_2O$ (**I**) has m.p. 71—72°. $N(CH_2\cdot CO_2H)_3$ (**II**) is converted by NaOH into $N(CH_2\cdot CO_2Na)_3$ (trilon *A*), (**III**), but by an excess of KOH into the K_2 H salt (**IV**). (**I**) and alkali-free $Cu(OH)_2$ in boiling H_2O afford the *salt*, $C_8H_{10}O_8N_2Na_2Cu,10H_2O$, m.p. 117° (decomp.) after softening at 70°, which is somewhat more stable than the Cu compound of glycine. Similarly (**III**) yields the complex salt, $C_{12}H_{12}O_{12}N_2Na_4Cu,4H_2O$, which is of the same order of stability; the corresponding Cu salt (+7H_2O and +1H_2O), decomp. ~222°, is described. $[CH_2\cdot N(CH_2\cdot CO_2Na)_2]_2$ (trilon *B*) (**V**) gives the *salt*, $C_{10}H_{12}O_8N_2Na_2Cu,4H_2O$ (**VI**), and the corresponding *Cu* salt (+4H_2O). Polarographic measurements show that Cu is retained in (**VI**) with remarkable firmness, thus explaining the use of (**V**) for removal of traces of Cu from fabrics. The stability of (**VI**) is ascribed to the presence of an ethylenic bridge. $(NH_2\cdot CH_2\cdot CO_2)_2Ca$ appears to be a normal Ca salt and gives an immediate ppt. with $(NH_4)_2C_2O_4$. Attempts to prepare a complex Ca salt of $NH(CH_2\cdot CO_2H)_2$ were unsuccessful. (**IV**) and $CaCO_3$ in boiling H_2O afford the complex *salt*, $C_{12}H_{12}O_{12}N_2K_4Ca,4H_2O$, which does not give an immediate ppt. with $(NH_4)_2C_2O_4$ or with Na stearate or soap solution; it is very easily decomposed by acids. The *salt*, $C_{12}H_{12}O_{12}N_2Ca_3$ (+4H_2O and anhyd.), is described. $[CH_2(N\cdot CH_2\cdot CO_2H)_2]_2$ is transformed by suitable quantities of KOH and $CaCO_3$ in boiling H_2O into the *salt*, $C_{10}H_{12}O_8N_2K_2Ca,4H_2O$, in which Ca is in such firm complex union that no turbidity is given with Na stearate or soap after many hr. A similar complex *Mg* salt (+5H_2O) is described. An explanation of the ability of (**III**) and (**V**) to soften H_2O is thus afforded. H. W.

Reaction of allylacetone and dry ammonium cyanide. A. V. Ipatov (*J. Gen. Chem. Russ.*, 1941, **11**, 605—607).—Allylacetone and NH_4CN in EtOH–HCl afford an unsaturated NH_2-*acid*, $C_7H_{13}O_2N$ (**I**), m.p. 231—234° (decomp.) [*picrate*, m.p. 175—177° (decomp.); *Bz* derivative, m.p. 125—127° (decomp.)], probably methylallylaminopropionic acid. G. A. R. K.

Polycondensation of peptide esters. I. Polyglycine esters. E. Pacsu and E. J. Wilson, jun. **II. Protein models. Preparation of tripeptide methyl esters.** E. J. Wilson, jun., and E. Pacsu (*J. Org. Chem.*, 1942, **7**, 117—125, 126—135).—I. Heating of the esters of simple peptides and the NH_2-acids may lead to intramol. removal of one mol. of EtOH from 1 mol. of acid ester, giving a diradical, $\cdot NH\cdot CHR\cdot CO\cdot$, two of which combine in inverted position to give the corresponding diketopiperazine. The ester of a dipeptide may lose 1 EtOH intramolecularly and the corresponding diketopiperazine is formed by ring-closure of the resulting $\cdot NH\cdot CHR\cdot CO\cdot NH\cdot CHR\cdot CO\cdot$ diradical. This cyclisation is very rapid in the case of glycylglycine ester, the dry crystals of which change into diketopiperazine even at room temp. in 10 days. A tripeptide ester may pass into a hexapeptide ester; an example is the intermol. elimination of one mol. of EtOH from 2 mols. of the tripeptide ester and union of the resulting $NH_2\cdot[CHR\cdot CO\cdot NH]_2\cdot CHR\cdot CO\cdot$ and $\cdot NH\cdot[CHR\cdot CO\cdot NH]_2\cdot CHR\cdot CO\cdot R'$ radicals. Tetrapeptide esters do not condense. Instead of cyclisation to give the simplest model of a "cyclol 6" postulated by the Wrinch theory, hexaglycylglycine Me ester, when heated, undergoes the type of condensation characteristic for the tripeptide esters in a series of successive reactions yielding 12-, 24-, 48- and 96-peptide esters of glycine (**I**). The course of the reaction has been followed by determining OMe in samples withdrawn at certain intervals of time. Similarly, the condensation reactions of the tripeptide and dodecapeptide esters of (**I**) proceed according to 3×2^n where n is an integer, giving 96 as the final stage of condensation. Analysis of the condensation products indicates that neither "cyclol 6" nor (probably) nonapeptide is formed when triglycylglycine Me ester is heated. The polypeptides obtained resemble denatured proteins and give strong biuret reactions. An improved prep. of diglycylglycine Me ester (**II**) is given. The prep. of pentaglycylglycine Me ester from (**II**) is described.

II. The action between NH_3 and α-bromo-propionyl- and -*iso*hexoyl-glycylglycine, α-bromopropionyl-leucylglycine, and chloroacetyl-leucylalanine is much more rapid than in Fischer's experiments and considerably improved yields are obtained in shorter times since the change is accompanied by elimination of HBr, formation of a corresponding OH-acid, and splitting of the peptide linking. Treatment of alanylglycyl-, leucylglycyl-, and alanylleucyl-glycine and glycyl-leucylalanine with MeOH–HCl under the conditions customary in esterification gives $NH_2\cdot CH_2\cdot CO_2Me,HCl$ and the hydrochlorides of the Me esters of alanylglycine, leucylglycine, alanyl-leucine, and leucylalanine. The tripeptide esters can be obtained, however, by using freshly prepared, saturated HCl–MeOH to insure rapid esterification and immediately pptg. the solutions with dry Et_2O or evaporating them at once in a vac. Thus are obtained dl-*alanylglycylglycine Me ester* (**III**), m.p. 86—88° [*hydrochloride*, m.p. 157—160° (corr.)]; dl-*leucylglycylglycine Me ester* (**IV**), m.p. 70° [*hydrochloride*, m.p. 227—228° (corr.; decomp.)]; *glycyl*-dl-*leucyl*-dl-*alanine Me ester*, m.p. 192—195° (*hydrochloride*). When heated, (**III**) and (**IV**) undergo condensation in a series of successive reactions apparently according to 3×2^n. The course of the reaction is followed by determination of OMe. Quant. analyses of the condensation products of (**III**) indicate that "cyclol 6" is not formed in the reaction. A definite conclusion could not be reached as to the formation or non-formation of a nonapeptide ester. The substances are sol. in H_2O and all give strong biuret reactions. H. W.

Biogenesis of pantothenic acid. R. Kuhn and T. Wieland (*Ber.*, 1942, **75**, [*B*], 121—123).—The suggested scheme is: $NH_2\cdot CHPr^{\beta}\cdot CO_2H \rightarrow Pr^{\beta}CO\cdot CO_2H$ (**I**) $\rightarrow$

$$(+CH_2O)\ OH\cdot CH_2\cdot CMe_2\cdot CO\cdot CO_2H \rightarrow \begin{matrix} CO\text{——}CO \\ | \quad\quad | \\ CMe_2\cdot CH_2 \end{matrix}\!\!>O \rightarrow$$

$$OH\cdot CH_2\cdot CMe_2\cdot CH(OH)\cdot CO_2H \rightleftharpoons \begin{matrix} OH\cdot CH\text{——}CO \\ | \quad\quad | \\ CMe_2\cdot CH_2 \end{matrix}\!\!>O +$$

$NH_2\cdot[CH_2]_2\cdot CO_2H \rightarrow OH\cdot CH_2\cdot CMe_2\cdot CH(OH)\cdot CO\cdot NH\cdot[CH_2]_2\cdot CO_2H$. (**I**) condenses with CH_2O in presence of K_2CO_3 to α-*keto*-ββ-*dimethyl*-γ-*butyrolactone* (**II**), m.p. 60°, hydrogenated to *dl*-α-hydroxy-ββ-dimethyl-γ-butyrolactone; the corresponding acid gives a sparingly sol. quinine salt, m.p. 183—184°. Addition of (**II**) to a fermenting mixture of yeast "M," glucose, and NaH_2PO_4 leads to (−)-α-hydroxy-ββ-dimethyl-γ-butyrolactone, m.p. 84—85°, $[\alpha]_D^{22}$ −50·5° in H_2O. H. W.

Analogues of pantothenic acid. I. Attempted preparation of growth promoters. II. Preparation of growth inhibitors. J. W. Barnett and F. A. Robinson (*Biochem. J.*, 1942, **36**, 357—363, 364—367; see also A., 1942, III, 621).—I. ββ-Dimethyl-γ-butyrolactone and $NH_2\cdot[CH_2]_2\cdot CO_2Na$ (**I**) in boiling abs. MeOH, with subsequent addition to Et_2O or $COMe_2$, give (impure) *Na deoxypantothenate* [*β-γ'-hydroxy-β'β'-dimethylbutyramidopropionate*]. Similarly, *β-hydroxy-γγ-dimethyl-δ-valerolactone* (+H_2O) (**II**), m.p. 126—126·5° [from $CH_2Br\cdot CO_2Et$, $OH\cdot CH_2\cdot CMe_2\cdot CHO$ (**III**), and Zn in C_6H_6 with subsequent hyrolysis (EtOH–KOH)], and (**I**) afford *Na homopanthothenate* [*β-β'δ'-dihydroxy-γ'γ'-dimethylvaleramidopropionate*], whilst *γγ-dimethyl-δ-Δ*$^{\alpha}$*-pentenolactone*, m.p. 115° [formed with another lactone from (**III**) and $CH_2(CO_2H)_2$ in Ac_2O–AcOH at 140°], and (**I**) give *Na dehydrohomopantothenate* [*β-δ'-hydroxy-γ'γ'-dimethyl-Δ*$^{\alpha'}$*-pentenoamidopropionate*]. γ-Butyrolactone or γ-valerolactone and (**I**) afford *Na bisnordeoxypantothenate* [*β-γ'-hydroxybutyramidopropionate*] or iso*nordeoxypantothenate* [*β-γ'-hydroxyvaleramidopropionate*], respectively, and with EtOH–$NHPh\cdot NH_2$ give the corresponding *phenylhydrazide*, m.p. 94—94·5° or 83—85°, respectively. Analogous compounds are prepared from α-hydroxy-ββ-dimethyl-γ-butyrolactone (**IV**) and the Ca salts of lysine, leucine, valine, and taurine.

II. (**IV**) and $NH_2\cdot[CH_2]_2\cdot SO_3Na$ (**V**) at 120° alone or in boiling

MeOH give " pantoyltaurine " [Na β-α′γ′-dihydroxy-β′β′-dimethylbutyramidoethanesulphonate]. Pantoyltauramide is prepared from (IV) and $NH_2{\cdot}[CH_2]_2{\cdot}SO_2{\cdot}NH_2$ at 120°. (II) and (V) at 120° afford " *homopantoyltaurine* " [*Na β-β′δ′-dihydroxy-γ′γ′-dimethylvaleramidoethanesulphonate*]. H. B.

Complex compounds of diguanide with tervalent metals. X. Hydroxo-aquo cobaltic bisdiguanidine and its salts. P. Rây and S. P. Ghosh (*J. Indian Chem. Soc.*, 1942, **19**, 1—8).—Co bisdiguanidine in aq. NH_3, when oxidised with air and treated with H_2SO_4, gives *diaminocobaltic bisguanidinium* sulphate ($+12H_2O$), and on further treatment affords *hydroxoaquocobaltic bisdiguanidinium sulphate* ($+2{\cdot}5H_2O$), which on addition of the appropriate reagent yields the *chloride* ($+H_2O$), *hydroxide* ($+H_2O$) [converted by heating into diol-tetrakisdiguanidine dicobalt), *nitrate*, *sulphite*, *dithionate* ($+H_2O$), and *thiosulphate* ($+H_2O$). When excess of $Na_2S_2O_3$ is added to the chloride, *thiosulphato-tetrakisdiguanidinium dithiosulphatodicobalt* ($+2H_2O$) is obtained. F. R. S.

II.—SUGARS AND GLUCOSIDES.

Sugar of cozymase.—See A., 1942, III, 641.

***l*-Sorbose. III. Further methyl derivatives of *l*-sorbose.** H. H. Schlubach and P. Olters (*Annalen*, 1942, **550**, 140—145; cf. A., 1940, II, 36).—β-Methyl-*l*-sorboside and TlOEt–EtOH, followed by MeI–Et_2O, afford *tetramethyl-β-methyl-*l*-sorboside*, b.p. 51°/0·01 mm., $[\alpha]_D^{20}$ +69·8° in $CHCl_3$, converted by dil. HCl at 90° into 1 : 3 : 4 : 5-*tetramethyl-*l*-sorbose*, b.p. 64°/0·08 mm., $[\alpha]_D^{20}$ −14·6° in $CHCl_3$. 2 : 3-*iso*Propylidene-1 : 4 : 6-trimethyl-*l*-sorbose, b.p. 135—137°/11 mm., $[\alpha]_D^{20}$ +29·6° in $CHCl_3$, and aq. AcOH yield 1 : 4 : 6-trimethyl-*l*-sorbose, which with MeOH–HCl, followed by aq. Me_2SO_4–NaOH–$COMe_2$, affords 1 : 2 : 3 : 4 : 6-*pentamethyl-*l*-sorbose*, b.p. 56° 0·01 mm., $[\alpha]_D^{20}$ −39·4° in $CHCl_3$, and thence (dil. HCl at 90°) 1 : 3 : 4 : 6-*tetramethyl-*l*-sorbose*, b.p. 64°/0·01 mm., $[\alpha]_D^{20}$ +29·7° in $CHCl_3$. A. T. P.

Preparation and rearrangement of phenylglucosides. (Miss) E. M. Montgomery, N. K. Richtmyer, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 690—694).—Prep. of α- (I) (64%), m.p. 115°, [α] +168·7° in $CHCl_3$, and β-phenyl-*D*-glucoside tetra-acetate (II) (85%), m.p. 125—126°, [α] −22·5° in $CHCl_3$, is improved. (II) is rearranged to (I) by $ZnCl_2$–PhOH at 120—125°/vac. Glucose α-penta-acetate, *p*-$NO_2{\cdot}C_6H_4{\cdot}OH$, and $ZnCl_2$ at 125° give α- (60%), m.p. 113°, [α] +200° in $CHCl_3$, and β-*p*-nitrophenyl-*D*-glucoside tetra-acetate (18%), m.p. 174—175°, [α] −41° in $CHCl_3$ [46 and 28%, respectively, from the β-penta-acetate], and thence α-, m.p. 216°, [α] +215° in H_2O, and β-*p*-nitrophenyl-*D*-glucoside, m.p. 164°, [α] −103·0° in H_2O. β-, $+H_2O$, m.p. 132°, [α] −83·0° in H_2O, and anhyd., m.p. 152°, [α] −106° in H_2O [tetra-acetate, m.p. 150—152°, [α] +45° in $CHCl_3$], and α-*o*-*nitrophenyl*-D-*glucoside*, m.p. 186—188°, [α] +206° in H_2O [tetra-acetate, m.p. 110° (lit. 95°), [α] +167° (lit. 124°) in $CHCl_3$], β-*p*-acetophenyl-*D*-glucoside tetra-acetate, m.p. 172—173°, [α] −28·6° in $CHCl_3$, α- (new), m.p. 145°, [α] +189° in H_2O (*triacetate*, m.p. 64—65°, [α] +135° in $CHCl_3$), and β-phenyl-*D*-xyloside, m.p. 179°, [α] −49·4° in H_2O (triacetate, m.p. 148°, [α] −50·5° in $CHCl_3$), are described. With $ZnCl_2$ and PhOH in 19 : 1 AcOH–H_2O at 120—125° various α-methylglucoside acetates give good yields of α-phenylglucosides (and some of the β-isomerides). [α] are $[\alpha]_D^{20}$. R. S. C.

Polysaccharide produced by the crown-gall organism. F. C. McIntire, W. H. Peterson, and A. J. Riker (*J. Biol. Chem.*, 1942, **143**, 491—496).—The apparently homogeneous *polysaccharide* (I), $[\alpha]_D^{25}$ −9° to −10° in H_2O, gives a triacetate, $[\alpha]_D^{25}$ +56° to +58·5° in $CHCl_3$. Hydrolysis of (I) yields only *d*(+)-glucose. A shift in rotation during hydrolysis indicates a predominance of β-linkings, and rate of hydrolysis and shape of hydrolysis curve suggest that the inner ring structures are exclusively pyranoside. Mol. wt. of (I) is 3600±200, corresponding with ~22 anhydroglucose units per mol. A. T. P.

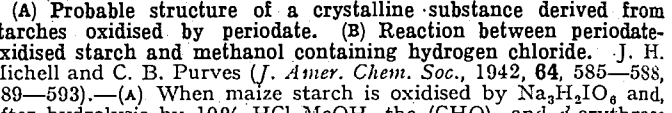
Starch. XVIII. Fractionation of native starch by dilute alcohol. K. H. Meyer and M. Fuld (*Helv. Chim. Acta*, 1941, **24**, 1408—1409).—The " cryst. amylose " obtained by Wiegel (A., 1942, II, 191) is a mixture of amylose and amylopectin. H. W.

Starch. XX. Viscosity of mucilage of starch. XXI. Amylolytic enzymes of yeast. XXII. Action of phosphorylase of potato. K. H. Meyer and P. Bernfeld (*Helv. Chim. Acta*, 1942, **25**, 391—398, 399—403, 404—405).—XX. Measurements of η of mucilages of various starches and of the solutions of the corresponding amyloses obtained after removing the grains by centrifuging support the view of Katz that the principal cause of η is the hydrodynamic effect produced by the suspended swollen grains. The conclusion is corroborated by the observation that η is diminished by the addition of any substance (NaCl, glucose, etc.) which diminishes the vol. occupied by the grains; this phenomenon is most marked with potato starch (I). The unique position of (I) is not due to chemical constitution, unusually high mol. wt., or outstanding size of grain but must be sought in the texture of the grain.

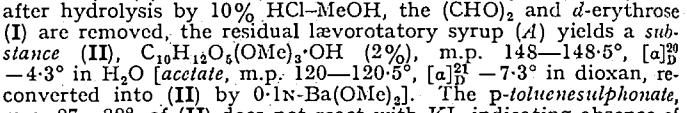
XXI. Details are given of the isolation from yeast of a phosphorylase (II) and amyloglucosidase (III) which hydrolyses starch (IV) and glycogen (V). (II) is capable of degrading (IV), (V), and residual dextrin (VI) which retains its action towards I. After a preliminary treatment by (II), (VI) is hydrolysed by β-amylase to a *dextrin II* which gives a colour with I. (II) appears to attack the non-aldehydic extremities of the chains. (III) degrades (VI) but the reaction with I is very persistent; it is not identical with α- or β-amylase.

XXII. Unlike yeast phosphorylase, the enzyme of potato has no action on (VI) in presence of PO_4'''. H. W.

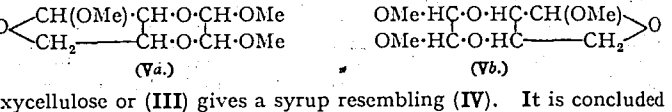
(A) Probable structure of a crystalline substance derived from starches oxidised by periodate. (B) Reaction between periodate-oxidised starch and methanol containing hydrogen chloride. J. H. Michell and C. B. Purves (*J. Amer. Chem. Soc.*, 1942, **64**, 585—588, 589—593).—(A) When maize starch is oxidised by $Na_3H_2IO_6$ and, after hydrolysis by 10% HCl–MeOH, the $(CHO)_2$ and *d*-erythrose (I) are removed, the residual lævorotatory syrup (*A*) yields a *substance* (II), $C_{10}H_{12}O_5(OMe)_3{\cdot}OH$ (2%), m.p. 148—148·5°, $[\alpha]_D^{20}$ −4·3° in H_2O [*acetate*, m.p. 120—120·5°, $[\alpha]_D^{21}$ −7·3° in dioxan, reconverted into (II) by 0·1N-$Ba(OMe)_2$]. The *p-toluenesulphonate*, m.p. 87—88°, of (II) does not react with KI, indicating absence of primary OH. In boiling 10% HCl–MeOH, (I) gives 82·5% of $[CH(OMe)_2]_2$ but no erythrose could be isolated. Hydrolysis and simultaneous HIO_3-oxidation of (II) is compatible with (II) being derived from 1 mol. of $(CHO)_2$ and 2 mols. of (I). (II) is thus probably



or



(B) The non-cryst. portion of *A* yields a syrup (III) (24%), b.p. 195—205°/3 mm., $[\alpha]_D$ −53·6° in H_2O, and a fraction (IV) (18%), b.p. 116—119·5°/3 mm. (IV) yields a substance (V*a* or *b*), $C_6H_7O_3(OMe)_3$, m.p. 97—98°, $[\alpha]_D$ −59·1° in H_2O, and a syrup, b.p. 117—118°/4 mm., $[\alpha]_D$ −91·7° in H_2O. In boiling 10% HCl–MeOH,



(V*a*.) (V*b*.)

oxycellulose or (III) gives a syrup resembling (IV). It is concluded that methanolysis of oxidised starch probably proceeds by random fission of acetal linkings and formation of new hemiacetal linkings leading to dioxans, but other structures are possible. M.p. are corr. R. S. C.

III.—HOMOCYCLIC.

Dehydration of *cyclo*propylmethylvinylcarbinol. A. P. Golovtschanskaja (*J. Gen. Chem. Russ.*, 1941, **11**, 608—615).—Acetyl*cyclo*propane and C_2H_2 in presence of powdered KOH and Et_2O at 0° afford cyclo*propylmethylacetylenylcarbinol* (I) (60—70%), b.p. 145—146°, and a fraction of b.p. 127—133°/6 mm., probably a mixture of glycols $C_{12}H_{18}O_2$, of which one is a solid, m.p. 85—86°. Electrolytic reduction of (I) affords 60—70% of cyclo*propylmethylvinylcarbinol* (II), b.p. 139°/751 mm. (II) when passed over anhyd. $MgSO_4$ at 240—250° gives 14—18% of β-cyclo*propylbutadiene* (III), oxidised by $KMnO_4$ to *cyclo*propanecarboxylic acid and $H_2C_2O_4$. (III) condenses with $(CH{\cdot}CO)_2O$ to a *product*, m.p. 83—84°, and is polymerised by Na to a solid and a syrupy liquid. G. A. R. K.

Thermal decomposition of five-membered rings. F. O. Rice and (Miss) M. T. Murphy (*J. Amer. Chem. Soc.*, 1942, **64**, 896—899).—Compounds containing 5-membered rings are thermally decomposed in accordance with predictions of the principle of least motion (A., 1938, II, 425). Succinic, maleic, citraconic, and itaconic anhydrides give CO, CO_2, and an unsaturated hydrocarbon. *cyclo*-Pentadiene, -pentene, -pentane, and methyl*cyclo*pentane yield a considerable variety of products. W. R. A.

Synthesis of 3-alkyl- or -aryl-Δ¹-*cyclo*hexenes. A. Berlande (*Compt. rend.*, 1941, **213**, 437—439).—Alkyl or aryl halide with Mg and 3-halogeno-Δ¹-*cyclo*hexene in Et_2O at 0° yields 3-methyl-, b.p. 104° (dibromide, b.p. 130°/35 mm.), 3-ethyl-, b.p. 131·5° (dibromide, b.p. 153°/45 mm., which with hot EtOH–NaOEt yields ethyl*cyclo*hexadiene, b.p. 136—137°), and 3-phenyl-Δ¹-*cyclo*hexene, b.p. 235° (dibromide decomposes when distilled, giving a diene, m.p. 66°), oxidised ($KMnO_4$) respectively to α-methyl-, -ethyl-, and -phenyl-adipic acids. A. Li.

Δ²:²′-Di*cyclo*hexenyl. A. Berlande (*Compt. rend.*, 1941, **213**, 484—486).—MgEtBr with 1-chloro-Δ²-*cyclo*hexene in dry Et_2O (ice-cooled) affords 15% of 1-ethyl-Δ²-*cyclo*hexene and 75% of Δ²:²′-di*cyclo*hexenyl, b.p. 236·5—237° (127°/30 mm.), which is oxidised (HNO_3) to *decane-αεζκ-tetracarboxylic acid*, m.p. 192—193° (decomp.). W. C. J. R.

Catalytic aromatisation of paraffin hydrocarbons. B. A. Kazanski (*J. Phys. Chem. Russ.*, 1940, **14**, 1330—1336).—Platinised C at 270—300° or Ni on Al_2O_3 at 350° transforms $Bu\beta_2$ into *p*-xylene etc. Presence of olefines deactivates the Pt on C. When 1 c.c. per hr. of

a paraffin mixture (C_7H_{10}—$C_{10}H_{22}$) is passed over 10 c.c. of an oxide catalyst, aromatisation takes place at 425—500°. The activity of Cr_2O_3 increases from "commercial" to "pptd. by NH_3 from aq. $Cr(NO_3)_3$" to "pptd. from aq. $Cr(NO_3)_3$ on ignited Cr_2O_3." The activity of these catalysts gradually decreases, especially if they have been used intermittently; heating in air followed by reduction with H_2 restores the activity. V_2O_5 and ThO_2 are inactive but the mixtures V_2O_5 1, Al_2O_3 10—20, and ThO_2 1, Al_2O_3 10 are efficient catalysts at 500°. ThO_2 may also be deposited on C. J. J. B.

Structure of naphthalene. J. K. Sirkin and M. E. Diatkina (*J. Gen. Chem. Russ.*, 1941, **11**, 626—646).—Theoretical. The reactions of $C_{10}H_8$ are discussed in the light of the theory of resonance between the different canonical structures. G. A. R. K.

Reactions of tetraphenyl*cyclo*pentadienone. Condensation with cyclic 1 : 3-diene systems. O. Grummitt, R. S. Klopper, and C. W. Blenkhorn (*J. Amer. Chem. Soc.*, 1942, **64**, 604—607).—Tetraphenyl-*cyclo*pentadienone [tetracyclone] (I) and *cyclo*pentadiene (II) in boiling C_6H_6 give 4 : 7-endo*carbonyl*-4 : 5 : 6 : 7-*tetraphenyl*-8 : 9-*dihydroindene* (III) (60%), m.p. 197—198° (*dibromide*, m.p. 222—223°). Under no conditions do 2 mols. of (I) condense with 1 mol. of (II) (cf. Dilthey *et al.*, A., 1935, 967). Thermal decomp. of (III) is complicated by dissociation into (I) and (II). Hydrogenation (PtO_2; C_6H_6–EtOH) of (III) gives 4 : 7-endo*carbonyl*-4 : 5 : 6 : 7-*tetraphenyl*-2 : 3 : 8 : 9-*tetrahydroindene*, m.p. 209—211°, which in boiling *p*-cymene (IV) gives CO and 4 : 5 : 6 : 7-*tetraphenyl*-(?2 : 3 : 8 : 9-)*tetrahydroindene*, m.p. 174—175°. Dehydrogenation, best by Se in boiling (IV), gives 4 : 5 : 6 : 7-*tetraphenylhydrindene*, m.p. 225—226°, oxidised by CrO_3–AcOH at 100° to 3 : 4 : 5 : 6 : 1 : 2-$C_6Ph_4(CO)_2O$ and some BzOH. (I) does not condense with furan, pyrrole, 1-methylpyrrole, or thiophen. R. S. C.

1 : 2-Diphenyl-3 : 4-dihydronaphthalene. (Miss) H. M. Crawford (*J. Amer. Chem. Soc.*, 1942, **64**, 727—728).—1 : 2-Diphenyl-3 : 4-dihydronaphthalene is dimorphic, the form of m.p. 76·5—77·5° slowly changing to that of m.p. 91·5—93·5° (cf. following abstract and A., 1939, II, 206). Prep. of the carbinol, m.p. 98·5—99°, was repeated. R. S. C.

Polyphenylnaphthalenes. I. 1 : 2-Diphenylnaphthalene. F. Bergmann, H. E. Eschinazi, and D. Schapiro. **II. 1 : 2 : 3-Triphenylnaphthalene.** F. Bergmann, D. Schapiro, and H. E. Eschinazi (*J. Amer. Chem. Soc.*, 1942, **64**, 557—558, 559—561).—I. $CH_2Bz{\cdot}CHPh{\cdot}CN$ and boiling HCl–EtOH give *Et γ-keto-αγ-diphenyl-n-butyrate*, b.p. 200—205°/1 mm., which with $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ gives a stable Al complex (which in CCl_4 gives a substance, m.p. 190°), decomposed by conc. H_2SO_4 to *αγ-diphenyl-γ-butyrolactone* (95%), m.p. 109—110°, b.p. 195—198°/0·5 mm. With red P in boiling HI this gives $Ph{\cdot}[CH_2]_2{\cdot}CHPh{\cdot}CO_2H$ (95%), m.p. 75°, b.p. 190°/1 mm., cyclised (Friedel–Crafts but not by P_2O_5–C_6H_6 and in poor yield by H_2SO_4–AcOH) to 1-keto-2-phenyl-1 : 2 : 3 : 4-tetrahydronaphthalene (90%), m.p. 82°. With MgPhBr this gives an oily carbinol, dehydrated by $KHSO_4$ at 160° to 1 : 2-diphenyl-3 : 4-dihydronaphthalene (57%), m.p. 94—95°, b.p. 210—215°/0·5 mm. Dehydrogenation (Se; 280—290°) gives 1 : 2-$C_{10}H_6Ph_2$ (I) (80%), m.p. 114° (*picrate*, m.p. 148°), and Li–Et_2O gives 1 : 2-*diphenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 183—184°/1·5 mm. [dehydrogenated by Se at ≮320° to (I)].

II. Prep. of, successively, $CH_2Ph{\cdot}COPh$, $CHPh{:}CPh{\cdot}COPh$, $CHPh{:}CPh{\cdot}CHPh{\cdot}OH$ [by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$], and $CHPh{:}CPh{\cdot}CHPh{\cdot}OMe$ (II) (by H_2SO_4–MeOH) is improved. With Na and later CO_2 in Et_2O at 0°, (II) gives *αβγ-triphenyl-Δ$^{\beta}$-n-butenoic acid* (III) (63%), m.p. 132—135° (does not react with Br; *Me*, m.p. 107°, and *Et* ester, m.p. 59°, b.p. 190—193°/0·3 mm.), $CHPh{:}CPh{\cdot}CH_2Ph$, m.p. 62°, b.p. 185—188°/0·03 mm. (gives a Br-adduct, which in ligroin yields 1 : 2-diphenylindene), and a neutral resin, b.p. 225—230°/0·03 mm. In conc. H_2SO_4, (III) gives exothermally 2 : 3-*diphenylhydrindene*-1-*carboxylic acid*, m.p. 161° (*Me* ester, m.p. 116—117°), and with H_2–Pd in dioxan gives with difficulty $H{\cdot}[CHPh]_3{\cdot}CO_2H$ (100%), m.p. 158° (*Me* ester, m.p. 158°; Na salt, m.p. 278—280°; *amide*, m.p. 168—169°), unchanged by conc. H_2SO_4 but with PCl_5–C_6H_6 giving a solid chloride, which with $AlCl_3$ in C_6H_6 at 0° gives 1-keto-2 : 3-diphenyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 146—147°, b.p. 205—207°/0·02 mm. MgPhBr at 100° then gives a carbinol, dehydrated by $KHSO_4$ at 160° to 1 : 2 : 3-*triphenyl*-3 : 4-*dihydronaphthalene* (52%), m.p. 176°, b.p. 215°/0·5 mm., which with Se at 280—300° gives 1 : 2 : 3-$C_{10}H_5Ph_3$ (70%), m.p. 153—154° (no picrate). R. S. C.

Molecular dissymmetry due to symmetrically placed hydrogen and deuterium. III. Attempted resolution of 4 : 4′-dibromo-2 : 3 : 5 : 6-tetradeuterobenzhydrylamine. Determination of deuterium in organic compounds. G. R. Clemo and G. A. Swan (*J.C.S.*, 1942, 370—374; cf. A., 1940, II, 40).—(p-$C_6H_4Br)_2CO$ and $HCO{\cdot}NH_2$ at 175° yield *form*-4 : 4′-*dibromobenzylhydrylamide*, m.p. 159°, converted by KOH–MeOH into 4 : 4′-*dibromobenzylhydrylamine*, m.p. 76° (*hydrochloride*; *d*-H tartrate, m.p. 210—211°, $[\alpha]_D^{18}$ +9·5° in MeOH; *d*-bromocamphorsulphonate, m.p. 260—262°, $[\alpha]_D^{18}$ +46·4° in MeOH). C_6D_5Br and p-$C_6H_4Br{\cdot}COCl$–$AlCl_3$–CS_2 give 4 : 4′-*dibromo*-2 : 3 : 5 : 6-*tetradeuterobenzophenone*, m.p. 172—173°, whence (as above) *form*-4 : 4′-*dibromo*-2 : 3 : 5 : 6-*tetradeuterobenzhydrylamide*, m.p. 158—159°, and 4 : 4′-*dibromo*-2 : 3 : 5 : 6-*tetradeuterobenzhydrylamine* (I), m.p. 75—76°. Attempted resolution of (I) through the *d*-H tartrate, m.p. 210—212°, $[\alpha]_D^{18}$ +9·3° in MeOH, or the *d*-bromocamphorsulphonate, m.p. 260—262°, $[\alpha]_D^{18}$ +45·9° in MeOH, was unsuccessful. The Harteck method (cf. A., 1938, I, 157) for determination of D is developed for the estimation of relative proportions of H and D in org. compounds. A. T. P.

Characterisation of carboxylic acids as ureides by means of carbodiimides. XII. Methiodides and methosulphates of *pp′*-tetramethyldiaminodiphenylcarbodi-imides. F. Zetzsche and G. Baum (*Ber.*, 1942, **75**, [*B*], 100—105; cf. A., 1940, II, 274).—$C(:N{\cdot}C_6H_4{\cdot}NMe_2$-$p)_2$ (I) and MeI in C_6H_6 yield the *monomethiodide* (II), m.p. 163—167°, converted by cold, saturated $H_2C_2O_4$ into *pp′-tetramethyldiaminodiphenylcarbamide methiodide*, decomp. 223—227°, and by H_2S in MeOH into the corresponding *thiocarbamide methiodide*, m.p. 190—192°. With 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2{\cdot}OH$, (II) gives a mixed *picrate-methopicrate*, m.p. 205—207° (decomp.) after softening at 180°. BzOH in $CHCl_3$ at room temp. and $CHPh{:}CH{\cdot}CO_2H$ in $COMe_2$ transform (II) into the *benz-*, m.p. 120—125°, and *cinnam-ureide*, m.p. 135—140°, respectively. (I) and MeI in $CHCl_3$ at room temp. and subsequently at 50° give the *dimethiodide*, m.p. 175—180° (decomp.) (softens at 150°), which evolves CO + CO_2 with $H_2C_2O_4$ and CO with HCO_2H. It is rapidly transformed by boiling H_2O into *pp′-tetramethyldiaminodiphenylcarbamide dimethiodide*, m.p. 206° (decomp.) (softens at 195°) (corresponding *dimethopicrate*, decomp. 189—196° after softening at 188°). The *thiocarbamide dimethiodide* decomposes at 185—187°. (I) and Me_2SO_4 in warm C_6H_6 afford the *monomethosulphate*, m.p. 155—158° (softens at 145°), from which are derived the *monomethosulphates* (+H_2O), m.p. 175—181° (softens at 170°), and (anhyd.) decomp. 188—190°, of the corresponding carbamide and thiocarbamide, respectively. Me_2SO_4 and (I) in $CHCl_3$ at room temp. yield the *dimethosulphate* of (I), rapidly converted by boiling H_2O into *pp′-tetramethyldiaminodiphenylcarbamide dimethosulphate*, m.p. 194—198° (corresponding *dipicrate*, m.p. 211°). H. W.

Phenylthiocarbamides. Triad –N·C·S–. XI. Oxidation of phenylthiocarbamide with copper sulphate, cupric chloride, copper nitrate, ferric chloride, and iodine. R. Sahasrabudhey and H. Krall (*J. Indian Chem. Soc.*, 1942, **19**, 25—29).—$CuSO_4$ and $CuCl_2$ are reduced by $NHPh{\cdot}CS{\cdot}NH_2$ (I) in acid media producing Hector's base (II); the reaction is independent of temp., concn., and dilution of the medium. Secondary reactions are the production of complexes (*A*) of (I) with Cu^{I} salts, the constitution of (*A*) being largely dependent on temp. $FeCl_3$ is reduced and gives (II) but no (*A*); $Cu(NO_3)_2$ and I similarly afford (II). F. R. S.

Complex compounds of diguanide with bivalent metals. III. Copper and nickel phenyldiguanidines and their different modifications. P. Rây and K. Chakravarty (*J. Indian Chem. Soc.*, 1941, **18**, 609—622).—Cu and Ni phenyldiguanidine, the hydrates and salts exist in α- and β-forms which are regarded as *cis–trans* isomerides, but may be dimorphs. Conditions for inter-conversion are described; the following are new: *α-Cu*, m.p. 155° (decomp.), *α-Ni* (+0·5H_2O), decomp. 255°, and *γ-Ni phenyldiguanidine* (+0·5H_2O) (considered to be a mixture of α- and β-), decomp. 263°; *α-Cu phenyldiguanidinium hydroxide, chloride*, m.p. 170° (decomp.) (*hexahydrate*, effervesces at 100°, resolidifying later with m.p. 210°), *bromide* (+2H_2O), *iodide* (+2H_2O), *nitrate, sulphate* (+4H_2O), *nitrite* (+H_2O), and *dithionate*; *β-Cu phenyldiguanidinium hydroxide, bromide* (+2H_2O), *iodide* (+2H_2O), *nitrate* (+H_2O), *nitrite*, and *dithionate* (+H_2O); *Cu phenyldiguanidinium sulphite, thiosulphate* (+2H_2O), *thiocyanate* (+H_2O), *chlorate, bromate*, and *iodate*; *Ni phenyldiguanidinium bromide* (+2H_2O), *iodide* (+H_2O), *dithionate, thiosulphate, nitrate* (+H_2O), *sulphite* (+H_2O), *chlorate, bromate, iodate* (+2H_2O), *thiocyanate*, and *nitrite* (+H_2O). F. R. G.

Interpretation of the Sandmeyer reaction. II. Corrections. H. H. Hodgson, S. Birtwell, and T. Walker (*J.C.S.*, 1942, 376—377; cf. A., 1942, II, 52). A. T. P.

Aralkylphenols.—See B., 1942, II, 253.

Branched-chain alkylphenylphenols.—See A., 1942, II, 253.

***N*-Dichlorocarbamates.**—See A., 1942, II, 217.

Stilbœstrol and related compounds.—See B., 1942, III, 171.

Molten alkali and benzenesulphonic acids. H. E. Fierz-David and G. Stamm (*Helv. Chim. Acta*, 1942, **25**, 364—370).—Only traces of m-$C_6H_4(OH)_2$ (I) in addition to PhOH are obtained by fusion of m-$C_6H_4(SO_3Na)_2$ with alkali under pressure; at 400° CO_2 is formed in 46% yield. In the "baking apparatus" at temp. up to 350° and with a 100% excess of alkali, pure (I) is obtained in 80% yield. With molten alkali p-$C_6H_4(SO_3Na)_2$ gives up to 5% of (I), very small yields of which are derived from p-$OH{\cdot}C_6H_4{\cdot}SO_3H$ or p-$C_6H_4Cl{\cdot}SO_3H$. At 280° p-$C_6H_4Cl{\cdot}OH$ is converted by alkali into PhOH with some $(C_6H_4{\cdot}OH)_2$ and HCO_2H. Baking appears to be inefficient for the conversion of $C_{10}H_7{\cdot}SO_3H$ and 2 : 6-$OH{\cdot}C_{10}H_6{\cdot}SO_3H$ into the OH-compounds. H. W.

Reaction between quinones and metallic enolates. XV. Structure of the chloromethylation product of trimethylquinol diacetate. L. I. Smith and R. B. Carlin (*J. Amer. Chem. Soc.*, 1942, **64**, 524—527).—The product obtained from 2 : 3 : 5 : 1 : 4-$C_6HMe_3(OAc)_2$, CH_2O, and HCl depends on the conditions, particularly the temp. At 0° it is mainly a substance, m.p. 228—229°, and at 15—20° mainly a substance, m.p. 167—168°. At 30° it is 6-*hydroxy*-3-*acetoxy*-2 : 4 : 5-*trimethylbenzyl chloride* (**I**) (89%), m.p. 150—151°, previously (A., 1939, II, 416) believed to be the 3 : 6-$(OAc)_2$-compound (**II**) (see below). The structure of (**I**) is shown by a positive Folin reaction, ready interaction with $AgNO_3$–MeOH, insolubility in aq. NaOH, by synthesis of (impure) 3 : 6 : 2 : 4 : 5 : 1-$(OH)_2C_6Me_3{\cdot}CH_2Cl$ (**III**), m.p. 114—115° (decomp.) (positive Folin test), and prep. of (**II**), m.p. 165° (negative Folin reaction; very slow interaction with $AgNO_3$–MeOH), from (**I**) or (**III**) by Ac_2O and a drop of H_2SO_4. Duroquinol is obtained from (**III**) by Zn dust in AcOH and duroquinone from (**II**) by $CHAcNa{\cdot}CO_2Et$–EtOH–H_2 followed by aq. $Cu(OAc)_2$ on the product. With $CHNa(CO_2Et)_2$ (**IV**) (1 mol.) in Et_2O at room temp. (2 hr.), (**I**) gives *Et*$_2$ 6-*hydroxy*-3-*acetoxy*-2 : 4 : 5-*trimethylbenzylmalonate* (**V**) (30%), m.p. 81—82° (positive Folin test), but on longer interaction or with slightly >1 mol. of (**IV**) gives Et 6-acetoxy-5 : 7 : 8-trimethyl-3 : 4-dihydrocoumarin-3-carboxylate (**VI**), m.p. 117—118°. (**V**) is accompanied by varying amounts (>50%) of *Et*$_2$ *di*-(6-*hydroxy*-3-*acetoxy*-2 : 4 : 5-*trimethylbenzyl*)*malonate*, m.p. 175° (positive Folin test). (**VI**) is also obtained from (**V**) by NaOH–Et_2O or from (**I**) and (**IV**) in Et_2O. R. S. C.

Bromination of 1 : 5-dihydroxy- and 1 : 5-diacetoxy-naphthalene, 5-methoxy-1-naphthol, and 1 : 5-dimethoxynaphthalene. A. H. Carter, E. Race, and F. M. Rowe (*J.C.S.*, 1942, 236—239).—1 : 5-$C_{10}H_6(OH)_2$ and Br–AcOH at 80° yield 2 : 6 : 1 : 5-$C_{10}H_4Br_2(OH)_2$, m.p. 224° (decomp.) (cf. Wheeler *et al.*, A., 1931, 215), converted by Me_2SO_4–aq. NaOH at 60° into the Me_2 ether, m.p. 160°, and 5 : 2 : 6 : 1-OMe·$C_{10}H_4Br_2$·OH, m.p. 150°. 1 : 5-$C_{10}H_6(OAc)_2$ similarly gives 2 : 4-*dibromo*-5-*acetoxy*-1-*naphthol* (**I**), m.p. 175° [the 1 : 5-*diacetate*, m.p. 131°, is stated by Willstätter *et al.* (A., 1928, 408) to be 4 : 8 : 1 : 5-$C_{10}H_4Br_2(OAc)_2$], hydrolysed by cold 0·4% aq. NaOH to 2 : 4 : 1 : 5-$C_{10}H_4Br_2(OH)_2$ (**II**), m.p. 153°. (**I**) and CH_2N_2–MeOH–Et_2O at −15° yield 2 : 4-*dibromo*-5-*acetoxy*-1-*methoxynaphthalene*, m.p. 121°, and thence (10% aq. NaOH) 6 : 8-*dibromo*-5-*methoxy*-1-*naphthol* (**III**), m.p. 112°. (**II**) and CH_2N_2 yield 2 : 4-*dibromo*-1 : 5-*dimethoxynaphthalene*, m.p. 88°. 5 : 1-OMe·$C_{10}H_5$·OH and Br–CCl_4 at 70° afford 2-*bromo*- (**IV**), m.p. 95°, or 2 : 8-*dibromo*-5-*methoxy*-1-*naphthol* (**V**), m.p. 130° (*acetate*, m.p. 133°); (**V**)–Me_2SO_4–aq. NaOH at 30° give 2 : 8-*dibromo*-1 : 5-*dimethoxynaphthalene*, m.p. 84°. 1 : 5-$C_{10}H_6(OMe)_2$ and Br–CCl_4 at 70° yield 4 : 8-*dibromo*-1 : 5-*dimethoxynaphthalene*, m.p. 187°. 2 : 6 : 1 : 5-$C_{10}H_4Br_2(OH)_2$ and CrO_3–AcOH at 85° give 2 : 6-dibromo-5-hydroxy-, m.p. 202°, and thence 6-bromo-2-anilino-5-hydroxy-1 : 4-naphthaquinone, m.p. 249°. 5 : 2 : 6 : 1-OMe·$C_{10}H_4Br_2$·OH, (**I**), (**IV**), or (**V**) is oxidised by CrO_3–AcOH to 2 : 6-*dibromo*-5-*methoxy*-, m.p. 177°, 2-*bromo*-5-*acetoxy*-, m.p. 158°, 2-*bromo*-5-*methoxy*-, m.p. 134°, or 2 : 8-*dibromo*-5-*methoxy*-1 : 4-*naphthaquinone*, m.p. 199°, respectively. (**V**) or (**III**) with aq. $KMnO_4$–NaOH, followed by H_2O_2, yields 5-*bromo*-, m.p. 212° (*phthalanil*, m.p. 232°), or 3 : 5-*dibromo*-6-*methoxyphthalic anhydride*, m.p. 140° (*phthalanil*, m.p. 191°), respectively. A. T. P.

Xenyl aryloxyalkyl ethers.—See B., 1942, II, 254.

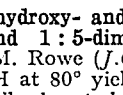
Duroquinol alkyl ethers.—See B., 1942, II, 254.

Method of preparing mono-ethers of methylene glycol. M. L. Gupta, R. Kaushal, and S. S. Deshapande (*J. Indian Chem. Soc.*, 1941, **18**, 638—640).—$CH_2Cl{\cdot}OAc$ with $CH_2Ph{\cdot}ONa$ in boiling C_6H_6 gives *benzyloxymethyl acetate*, b.p. 152—155°/29, mm., hydrolysed with 10% KOH in EtOH to *formaldehyde monobenzyl acetal*, b.p. 75—77°/4 mm. (*phenylurethane*, m.p. 75°). $CH_2Cl{\cdot}OMe$ with $CH_2Ph{\cdot}ONa$ yields *formaldehyde Me benzyl acetal*, b.p. 84—87°/8 mm., together with a compound, b.p. 165—167°/8 mm. F. R. G.

Phenol–formaldehyde resins. VIII. Mode of formation of phenolic aldehydes during the hardening of phenolic alcohols. K. Hultzsch (*Ber.*, 1942, **75**, [*B*], 106—114).—Further evidence is presented in favour of the view that quinonemethides are intermediates in the conversion of phenolic alcohols into aldehydes etc., and that the change does not necessarily take place through polymeric forms. Trimeric 2 : 3 : 5 : 1-O:$C_6H_2Me_2$:CH_2 [3 : 5-dimethyl-*o*-benzoquinonemethide] at 250° gives very small amounts of 2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CHO, mesitol, 2 : 3 : 5 : 1-$(OH{\cdot}C_6H_2Me_2{\cdot}CH_2)_2$, and a dark resin. At 230° dimeric 3-methyl-5-*tert.*-butyl-*o*-benzoquinonemethide gives similarly the expected aldehyde, phenol, and C_2H_6 derivative. Analogous results are obtained with 5-*cyclo*hexyl-3-methyl-*o*-benzoquinonemethide. Attempts to resinify di-2-acetoxy-3-methyl-5-*tert.*-butylbenzyl ether were unsuccessful. 2 : 3 : 5 : 1-OH·$C_6H_2Cl_2{\cdot}CH_2{\cdot}$OH (**I**) is unchanged by HCl in Et_2O at room temp. or PhMe at the b.p. and is converted by HCl in AcOH into 2 : 3 : 5 : 1-OAc·$C_6H_2Cl_2{\cdot}CH_2{\cdot}$OH, m.p. 115°. At 205°, (**I**) affords (?) trimeric 3 : 5-*dichloro*-*o*-*benzoquinonemethide* (+3C_6H_6), m.p. 278—280° (decomp.) after darkening at 260°. H. W.

Preparation of 1- and 2-indanol and their derivatives from indene. W. F. Whitmore and A. I. Gebhart (*J. Amer. Chem. Soc.*, 1942, **64**, 912—917).—Indene bromohydrin (**I**) in aq. MeOH–KOH in dioxan at room temp. gives indene oxide (100%), reduced by H_2–Raney Ni to 2-indanol (65%), also obtained directly from (**I**) by H_2–Raney Ni in KOH–EtOH. With boiling Ac_2O–NaOAc, (**I**) gives the glycol diacetate. BzCl–C_5H_5N–dioxan at 0°—room temp. converts (**I**) into the *benzoate*, m.p. 104°, which with 0·5N-KOH–EtOH at room temp. gives KBr, EtOBz, and indene glycol. Addition of chloroindane (**II**) to NaOAc–AcOH–H_2O at 98° gives mainly 1-indanyl acetate (**III**) (86%) and 1-indanol (**IV**) (14%), whence boiling N-KOH–EtOH yields (**IV**), *forms*, m.p. 40·5° (unstable) and 52·5°. (**IV**) is also obtained from indan-1-one or (**I**) by H_2–Raney Ni–H_2PtCl_6–NaOH [or –$Mg(OH)_2$] in EtOH. With boiling HCl–EtOH–H_2O, (**IV**) gives 1-*indanyl Et ether* (**V**), b.p. 78—80°/2 mm., reaction proceeding by way of (**II**), which also gives (**V**) when boiled with $CaCO_3$–EtOH. With conc. HCl in boiling dioxan, (**IV**) gives *di*-1-*indanyl ether*, *forms*, m.p. 68° and 74°, also obtained from (**IV**), (**II**), and $CaCO_3$ in dioxan. 1-*Indanyl benzoate*, m.p. 63°, p-*nitrobenzoate*, m.p. 75°, and α-*naphthylurethane*, *forms*, m.p. 137° and 145°, and 2-*indanyl benzoate*, m.p. 63°, p-*nitrobenzoate*, m.p. 139°, and α-*naphthylurethane*, m.p. 191°, are described. M.p. are on a Dennis-Shelton bar. R. S. C.

Organic osmium compounds. II. R. Criegee, B. Marchand, and H. Wannowius (*Annalen*, 1942, **550**, 99—133; cf. A., 1936, 603).—OsO_4 and MeOH–KOH (or –CsOH) yield K_2 (**I**) (or Cs_2) *tetramethylosmiate*, $Os(OMe)_4(OK)_2$, converted by warm AcOH into *K* (or *Cs*) *triacetylosmiate*, $OsO(OAc)_3OK$ (+2AcOH, lost at 60°/0·5 mm.). EtOH–C_5H_5N and OsO_4 in *cyclo*hexane at room temp. for 2—3 days give the *complex* (**II**), $OsO_3,2C_5H_5N$; in absence of EtOH at 0°, the *complex*, OsO_4,C_5H_5N, results. *trans-cyclo*Hexane-1 : 2-diol and (**I**) in KOH–MeOH yield K_2 *di*-(trans-cyclo*hexane*-1 : 2-*diol*)*osmiate*, $C_{12}H_{20}O_6K_2Os$, and thence (dil. H_2SO_4 in CH_2Cl_2) *di*-(trans-cyclo*hexane*-1 : 2-*diol*)*osmiate*, $C_{12}H_{20}O_5Os$; K_2 *di*-(trans-cyclo*heptane*-1 : 2-*diol*)*osmiate*, *di*-(cis- and trans-cyclo*heptane*-1 : 2-*diol*)-, and *diethylene glycol-osmiate* are also prepared. $\Delta^{1:3}$-*cyclo*Pentadiene and



(*A*.)

Et_2O–OsO_4 afford cyclo*pentenediolosmiate*, $C_5H_6O_4Os$ (type *A*); and α-pinene yields *pinene glycolosmiate*, $C_{10}H_{16}O_4Os$, decomp. 169°. Similar *monoesters* are obtained from CMe_2:CMe_2, CHPh:CH·COPh, CMe_2:CH·COMe, *cyclo*pentene, 1 : 2-dimethyl*cyclo*hexene, camphene, limonene, Δ^1-dihydronaphthalene, cholesterol, and ergosterol. $\Delta^{1\ 3}$-*cyclo*Hexadiene, *cyclo*heptene, or phenanthrene and OsO_4 in C_5H_5N–Et_2O or –C_6H_6 afford Δ^3-cyclo*hexene*-1 : 2-*diolosmiate* (+2C_5H_5N), cyclo*heptanediolosmiate* (+2C_5H_5N), or 9 : 10-*dihydrophenanthrene*-9 : 10-*diolosmiate* (+2C_5H_5N), respectively. Similar *esters* (all +2C_5H_5N) are obtained from C_2H_4, CMe_2:CMe_2, *cyclo*pentadiene, di*cyclo*pentadiene, *cyclo*hexene, CPh_2:CPh_2, $(CPh_2{:}CH{\cdot})_2$, camphene, stilbene, limonene, cholestenone, cholesterol, ergosterol, Δ^1-dihydronaphthalene, di(diphenylene)-ethylene, and CHPh:CH·COPh; tolan gives the *ester*, $C_{14}H_{10}O_8Os_2,4C_5H_5N$. Some of the esters are also prepared from the corresponding diol and (**II**); other *esters* (+2C_5H_5N) are obtained from (**II**) and *cis-cyclo*pentanediol, *cis*- and *trans-cyclo*hexane- and -*cyclo*heptane-diol, *cis*-hydrindenediol, *cis*-acenaphthenediol, *cis*-dimethyl- and -diphenyl-acenaphthenediol, *cis*-diphenyldihydrophenanthrenediol, and *o*-$C_6H_4(OH)_2$. Similar *esters* (all + 1 mol. of 2 : 2′-dipyridyl) are prepared from *cyclo*hexene, *cyclo*hexadiene, limonene, α-pinene, Δ^1- and Δ^2-dihydronaphthalene, sorbaldehyde, CMe_2:CH·COMe, CHPh:CH·COPh, and cholestenone. Stilbene, limonene, or C_2H_2 and OsO_4 in Et_2O–quinoline give the *adducts*, $C_{14}H_{12},OsO_4,2C_9H_7N$, or $C_{10}H_{16},OsO_4,2C_9H_7N$, or $C_2H_2,2OsO_4,4C_9H_7N$, respectively. The esters (or their C_5H_5N compounds) from *cyclo*pentadiene or *cyclo*hexadiene are hydrolysed by aq. K_2CO_3 or KOH (usually in presence of mannitol), and thence hydrogenated (PtO_2) to *cis-cyclo*-pentane- or -hexane-1 : 2-diol, respectively. Phenanthrene–OsO_4–$2C_5H_5N$ and aq. KOH–mannitol afford cis-9 : 10-*dihydrophenanthrene*-9 : 10-*diol*, m.p. 178—179° (corr.) [*diacetate*, m.p. 109° (corr.)]. The adduct ergosterol–OsO_4–$2C_5H_5N$ and aq. KOH–mannitol give ergostadiene-3 : 5 : 6-triol (*cis*-configuration), m.p. 244°, converted by $Pb(OAc)_4$ into the ketoaldehyde, m.p. 155—157° (cf. Heilbron *et al.*, A., 1933, 500). A. T. P.

Condensation of *o*-, *m*-, and *p*-nitrobenzaldehydes with malonic acid in presence of organic bases. D. S. Mittal (*J. Indian Chem. Soc.*, 1942, **19**, 47—48).—The nitrocinnamic acids are obtained in 75—90% yields from 1 mol. of aldehyde, 1 mol. of $CH_2(CO_2H)_2$, and 0·15 mol. of C_5H_5N, piperidine, or quinoline at 100° (bath). F. R. S.

Condensation of aldehydes with malonic acid in presence of organic bases. XIV. Condensation of 2 : 4-dinitrobenzaldehyde; influence of nitro-groups. K. C. Pandya, P. I. Ittyerah, and (Miss) R. K. Pandya (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 78—82).—Under mild conditions reaction between 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}$CHO and $CH_2(CO_2H)_2$ does not appear to occur and traces of C_5H_5N, piperidine (**I**), and lutidine bring little advantage. Higher temp. and longer periods of heating and use of a mixture of C_5H_5N and (**I**) invariably lead to decomp., charring, and resinification. The best

yields (50%) of 2 : 4 : 1-$(NO_2)_2C_6H_3$·CH:CH·CO_2H, m.p. 179°, are secured by heating the reactants with C_5H_5N for 4 hr. at 100° (bath) and for a further 4 hr. at 105—110° (bath). The cause of the diminished activity of CHO by two NO_2-groups at $C_{(2)}$ and $C_{(4)}$ is unexplained. H. W.

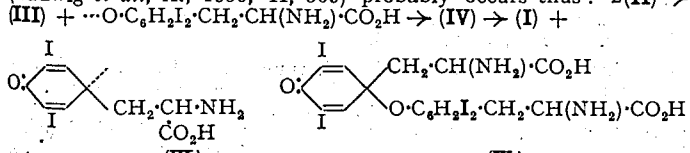
Unsymmetrical cyanostilbenes. J. B. Niederl and A. Zicring (*J. Amer. Chem. Soc.*, 1942, **64**, 885—886).—RCHO, NHAc·CH_2·CO_2H, and NaOAc give azlactones (30—40%), R (here and below) = *p*-OMe·C_6H_4, m.p. 114°, 3 : 4-$(OMe)_2C_6H_3$, m.p. 167°, and 3 : 4-CH_2O_2:C_6H_3, m.p. 181°, hydrolysed by boiling aq. NaOH to CHR:C(NHAc)·CO_2H, m.p. 216°, 208°, and 219°, respectively, and then by boiling aq. acid to CH_2R·CO·CO_2H (~90%), m.p. 184°, 185°, and 213°, respectively. The oximes, m.p. 159°, 164°, and 170°, respectively, thereof in Ac_2O give CH_2R·CN (50—70%), b.p. 120°/4 mm., 183°/16 mm., and 160°/10 mm., respectively, which with R'CHO in warm 95% EtOH–NaOEt give, usually, excellent yields of CN·CR:CHR'. *α-Cyano-4-methoxy-*, m.p. 94°, *-3 : 4-*, m.p. 87°, *-4 : 2'-*, m.p. 98°, and *-4 : 4'-dimethoxy-*, m.p. 108°, and *-3 : 4-methylenedioxy-*, m.p. 125°, *2'-*, m.p. 129°, and *4'-chloro-α-cyano-4-methoxy-*, m.p. 110°, *2'-*, m.p. 113°, and *4'-chloro-α-cyano-3 : 4-dimethoxy-*, m.p. 115°, *2'-*, m.p. 135°, and *4'-chloro-α-cyano-3 : 4-methylenedioxy-*, m.p. 130°, *3'-nitro-α-cyano-4-methoxy-*, m.p. 159°, *-3 : 4-dimethoxy-*, m.p. 166°, and *-3 : 4-methylenedioxy-*, m.p. 195°, *α-cyano-4-methoxy-4'-methyl-*, m.p. 97°, *α-cyano-3 : 4-dimethoxy-4'-methyl-*, m.p. 112°, *α-cyano-3 : 4-methylenedioxy-4'-methyl-*, m.p. 122°, *α-cyano-4 : 3' : 4'-*, m.p. 105°, *-3 : 4 : 2'-*, m.p. 87°, and *-3 : 4 : 4'-trimethoxy-*, m.p. 129°, *α-cyano-3 : 4 : 3' : 4'-tetramethoxy-*, m.p. 155°, *α-cyano-4-methoxy-3' : 4'-methylenedioxy-*, m.p. 129°, and *-2'-*, m.p. 102°, and *-4'-methoxy-3 : 4-methylenedioxy-*, m.p. 129°, *α-cyano-3 : 4-dimethoxy-3' : 4'-methylenedioxy-*, m.p. 150°, and *-3' : 4'-dimethoxy-3 : 4-methylenedioxy-*, m.p. 144°, *α-cyano-3 : 4 : 3' : 4'-bismethylenedioxy-*, m.p. 185°, and *α-cyano-4'-dimethylamino-4-methoxy-*, m.p. 149°, *-3 : 4-dimethoxy-*, m.p. 121°, and *-3 : 4-methylenedioxy-*, m.p. 169°; *-stilbene* are described. These have feeble œstrogenic properties. R. S. C.

Nitration of *p*-iodophenylacetic acid. S. N. Slater (*New Zealand J. Sci. Tech.*, 1941, **23**, B, 15—16).—*p*-C_6H_4I·CH_2·CO_2H and KNO_3 added to conc. H_2SO_4–AcOH give ~85% of 3 : 4 : 1-NO_2·C_6H_3I·CH_2·CO_2H, m.p. 122—123° (also formed, less well, using H_2SO_4–HNO_3), oxidised ($KMnO_4$) to 3 : 4 : 1-NO_2·C_6H_3I·CO_2H.
M. H. M. A.

Synthetic anthelmintics. II. γ-Substituted butyrolactones. III. γγ-Disubstituted butyrolactones. J. J. Trivedi and K. S. Nargund (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 99—101, 102—105).—II. *β-o-Anisoylpropionic acid*, m.p. 98° (*Ag* salt; *Me*, b.p. 160°/3 mm., and *Et*, b.p. 170°/7 mm., ester), obtained from the OH-acid, Me_2SO_4, and 10% NaOH, is reduced (Na–abs. EtOH at 100°) and then lactonised by boiling 15% H_2SO_4 to *γ-o-anisylbutyrolactone*, b.p. 170°/16 mm. Similarly, *β-3-methoxy-p-toluoylpropionic acid*, m.p. 126° (sol. Ca and insol. Ba and Zn salts; *Me*, b.p. 190—192°/14 mm., and *Et*, m.p. 76°, ester), is converted into *γ-3-methoxy-p-tolylbutyrolactone*, b.p. 197—198°/9 mm., hydrolysed to *γ-hydroxy-γ-3-methoxy-p-tolylbutyric acid*, m.p. 114°. *γ-3 : 4-*, m.p. 120—121°, and *γ-2 : 5-*, m.p. 94—95°, *-dimethoxyphenylbutyrolactone* are described.

III. The requisite keto-ester is treated with the appropriate Grignard reagent; the product is hydrolysed and, after removal of neutral impurities, lactonised by hot 15% H_2SO_4. Thus are obtained: *γ-phenylvalerolactone*, b.p. 145—147°/5 mm.; *γ-hydroxy-γ-phenylvaleric acid*, m.p. 106°; *γ-phenylhexolactone*, b.p. 160°/16 mm.; *γ-hydroxy-γ-phenyl-n-hexoic acid*, m.p. 102—103°; *γ-phenylheptolactone*, b.p. 145—150°/20 mm.; *γ-phenyloctolactone*, b.p. 173—174°/10 mm.; *γγ-diphenylbutyrolactone*, m.p. 90—91°; *γ-hydroxy-γγ-diphenylbutyric acid*, m.p. 141°; *γ-p-anisylvalerolactone*, b.p. 215—220°/42 mm.; *γ-hydroxy-γ-p-anisylvaleric acid*, m.p. 120°; *γ-p-anisyl-hexolactone*, b.p. 180—185°/5 mm. (corresponding *γ-OH-acid*, m.p. 123°), *-heptolactone*, b.p. 215—217°/20 mm., *-δ-methylhexolactone*, b.p. 190°/12 mm., *-octolactone*, b.p. 220—225°/15 mm., *-ε-methylheptolactone*, b.p. 200—205°/22 mm., *-ζ-methyloctolactone*; b.p. 205—210°/15 mm., and *-decolactone*, b.p. 215—220°/7 mm. *Et β-p-anisoylpropionate* has m.p. 57°. H. W.

Oxidation of 3 : 5-di-iodotyrosine to thyroxine. T. B. Johnson and L. B. Tewkesbury, jun. (*Proc. Nat. Acad. Sci.*, 1942, **28**, 73—77).—The production of thyroxine (I) from 3 : 5-di-iodotyrosine (II) [Ludwig *et al.*, A., 1939, II, 369) probably occurs thus: 2(II) → (III) + ···O·$C_6H_2I_2$·CH_2·CH(NH_2)·CO_2H → (IV) → (I) +



(III.) (IV.)

CH_2:C(NH_2)·CO_2H → NH:CMe·CO_2H → NH_3 + $AcCO_2H$.
R. S. C.

Preparation of *p*-alkyl-substituted benzoic acids. A. Zaki and H. Fahim (*J.C.S.*, 1942, 307—308).—PhAlk-*n* and AcCl–$AlCl_3$ in light petroleum at 0°—room temp., and then at 100° (bath), afford the *p*-C_6H_4Alk·COMe, oxidised (NaOBr) to *p*-C_6H_4Alk·CO_2H. *p-n*-Butyl-, b.p. 268—270°/766 mm. (*oxime*, m.p. 43—44°; *semicarbazone*, m.p. 182—183°; p-*nitrophenylhydrazone*, m.p. 151—152°), *p-n*-amyl-, b.p. 145°/11 mm. (*oxime*, m.p. 62—63°; *semicarbazone*, m.p. 180—181°; p-*nitrophenylhydrazone*, 149—150°), *p-n*-hexyl-, b.p. 158°/12 mm. (*oxime*, m.p. 45—46°; *semicarbazone*, m.p. 178°; p-*nitrophenylhydrazone*, m.p. 135°), *p-n*-heptyl-, b.p. 160—163°/7 mm. (*oxime*, m.p. 41—42°; *semicarbazone*, m.p. 176°; p-*nitrophenylhydrazone*, m.p. 140°), and *p-n*-octyl-acetophenone, b.p. 165—168°/4 mm. [oxime, m.p. 52—53° (lit. 43°); *semicarbazone*, m.p. 174°; p-*nitrophenylhydrazone*, m.p. 127°], afford p-n-*butyl-*, m.p. 101°, *-amyl-*, m.p. 88°, *-hexyl-*, m.p. 97°, *-heptyl-*, m.p. 101·5°, or *p-n*-octylbenzoic acid, m.p. 99—100° (lit. 139°), respectively. A. T. P.

Substituted amides of mesitoic acid. R. G. Kadesch (*J. Amer. Chem. Soc.*, 1942, **64**, 726).—*Mesit-ethyl-*, m.p. 114·5—115·5°, *-isopropyl-*, m.p. 113·5—115°, *-benzyl-*, m.p. 137·5—138·5°, and *-α-phenylethyl-amide*, m.p. 130—131°, *-o-*, m.p. 124—125·5°, *-m-*, m.p. 110—111·5°, and *-p-toluidide*, m.p. 173—174°, *-p-anisidide*, m.p. 185°, *-p-phenetidide*, m.p. 171—172°, *-o-tert.-butylanilide*, m.p. 150·5—152°, *-β-naphthalide*, m.p. 165—166·5°, *-piperidide*, m.p. 75·5—77°, and *-morpholide*, m.p. 70—71·5°, are prepared from the chloride and amine in C_6H_6. R. S. C.

Preparation of 3 : 5-dinitrobenzoic acid and 3 : 5-dinitrobenzoyl chloride. Acylation of amino-acids by 3 : 5-dinitrobenzoyl chloride and other acid chlorides. B. C. Saunders, G. J. Stacey, and (in part) I. G. E. Wilding (*Biochem. J.*, 1942, **36**, 368—375; cf. Town, A., 1941, II, 213).—Prep. of 3 : 5 : 1-$(NO_2)_2C_6H_3$·CO_2H and 3 : 5 : 1-$(NO_2)_2C_6H_2$·COCl (I), new m.p. 69·5°, is improved. Reaction between various ArCOCl and a slight excess of N-NaOH shows that (I) and *p-* and *m*-NO_2·C_6H_4·COCl (II) are completely hydrolysed within 2 min.; $AlkSO_2Cl$ are similarly very reactive whilst $ArSO_2Cl$ are not. The relative merits of (I) and other chlorides as acylating agents for NH_2-acids are discussed. With NH_2Ph in EtOAc, (I) and BzCl give 95 and 78%, respectively of NH_2Ph,HCl (not formed using *p*-C_6H_4Me·SO_2Cl or $MeSO_2Cl$) after 2 min. The following are prepared in N-NaOH: dl-*α-3 : 5-dinitrobenzamido-n-valeric*, m.p. 227·5—228·5° (decomp.), *-n-hexoic* m.p. 203·5—204°, and *-α-methyl-n-butyric acid*, m.p. 186°; 3 : 5-dinitrobenzoylglycine, new m.p. 179·5°; *Me o-3' : 5'-dinitrobenzoyloxybenzoate*, m.p. 107·5°; *m*-nitrobenzoylglycine, new m.p. 166° [from (II)]; 3 : 5-*dinitrobenzenesulphonylglycine*, m.p. 191—192°; methanesulphonyl-glycine, m.p. 172—173°, and *-anthranilic acid*, m.p. 190·5—191·5°; *Ph*, m.p. 59·5°, and p-NO_2·C_6H_4, m.p. 93—93·5°, *methanesulphonate*; *α-toluenesulphonylglycine*, m.p. 152° *Na* 3 : 5-*dinitrobenzene-* and *α-toluene-sulphonate*. dl-OH·CHPh·CO_2H does not react with (I) in N-NaOH. 3 : 5-Dinitrobenzoyl derivatives of some NH_2-acids may exist in different forms (cf. *loc. cit.*). H. B.

Separated auxo-enoid systems. XV. Colour of *p*-nitro- and 3 : 5-dinitro-benzoates of phenols containing an additional auxo-group. V. A. Izmailski and A. V. Belotzvetov (*J. Gen. Chem. Russ.*, 1941, **11**, 650—660).—The colour of *p*-nitro- and 3 : 5-dinitro-benzoates of a series of phenols is explained by assuming an intra- or, more probably, an inter-mol. interaction (complex formation) between a nitro-enoid and an auxo-enoid system, as in the corresponding arylamides (A., 1937, II, 239). The *p*-nitrobenzoates are coloured only if the phenol contains a powerful auxochrome (*e.g.*, NMe_2) *para* to OH, but OMe or NHAc in this position is sufficient to cause colour in the dinitrobenzoates. Di-esters of quinol are colourless. The following are described: p-*anisyl*, m.p. 115·2—115·8°, *p*-NMe_2·C_6H_4, m.p. 176—177°, p-*acetamidophenyl* (I), m.p. 216·2—216·8°, and p-*hydroxyphenyl*, m.p. 192—193·5°, p-*nitrobenzoates*; p-*anisyl*, m.p. 166—166·5°, p-*dimethylaminophenyl*, m.p. 206·5—207°, p-*acetamidophenyl* (II), m.p. 212·5—213·2°, and p-*hydroxyphenyl*, m.p. 169—170·5°, 3 : 5-*dinitrobenzoates*. *Quinol di-3 : 5-dinitrobenzoate* has m.p. 329—330°. p-p'-*Nitrobenzamidophenyl acetate*, m.p. 234·5—235·5°, is not identical with (I) and is hydrolysed to *p-p'*-nitrobenzamidophenol; the corresponding 3 : 5-*dinitrobenzoyl* compound differs from (II) and is hydrolysed to *N*-3 : 5-dinitrobenzoyl-*p*-aminophenol. G. A. R. K.

Rearrangement of 3 : 5-dichloro-*O*-crotylsalicylic acid and related compounds. D. S. Tarbell and J. W. Wilson (*J. Amer. Chem. Soc.*, 1942, **64**, 607—612).—2 : 3 : 5 : 1-OH·$C_6H_2Cl_2$·CO_2Me (I) with CHMe:CH·CH_2Br (II) and K_2CO_3 in boiling COMeEt and later KOH–MeOH–H_2O gives 3 : 5-*dichloro-2-crotyloxybenzoic acid* (III) (>58%), m.p. 121·5—122·5°, oxidised by aq. $KMnO_4$ to (?) an anhydride, decomp. 257—259°, of 2 : 4-*dichloro-6-carboxyphenoxyacetic acid* (IV) (53%), m.p. (from 3N-HCl) 210—211°, and converted at 130—131° in CO_2 into 2 : 4-dichloro-6-α-methylallylphenol (V) (58%), b.p. 95—98°/5 mm. (*phenylurethane*, m.p. 103—104°), 2 : 3 : 5 : 1-OH·$C_6H_2Cl_2$·CO_2H (20%), and a fraction (5%), b.p. ~150°/5 mm. CH_2Br·CO_2Et, (I), and NaOMe–MeOH give a diester, m.p. 57—59°, hydrolysed by 30% KOH–MeOH to (IV). Hydrogenation (PtO_2) of (V) in EtOH gives 2 : 4-dichloro-6-*sec.*-butylphenol (VI), b.p. 142°/22 mm. (*phenyl-*, m.p. 114—115°, and *α-naphthyl-urethane*, m.p. 151—153°), also obtained thus: 2 : 4 : 1-$C_6H_3Cl_2$·OH → (Ac_2O–C_5H_5N) -$C_6H_3Cl_2$·OAc, b.p. 133—134°/22 mm. → ($AlCl_3$; 135—145°) 2 : 3 : 5 : 1-OH·$C_6H_2Cl_2$·COMe, m.p. 94—96° → ($MgEtBr$–Et_2O) *β-3 : 5-dichloro-2-hydroxyphenylbutan-β-ol* (68%), m.p. 108—109° →

(heat + trace of I) ? 2 : 3 : 5 : 1-OH·$C_6H_2Cl_2$·CMe:CHMe (86%), b.p. 140—142°/25 mm. → (H_2–Pt) (**VI**). At ~175—180° *o*-CH_2:CH·CH_2·O·C_6H_4·CO_2H gives 3 : 2 : 1-CH_2:CH·CH_2·C_6H_3(OH)·CO_2H (64%) and *o*-allylphenol (23%). 2 : 3 : 5 : 1-CH_2:CH·CH_2·O·$C_6H_2Cl_2$·CO_2H rearranges more slowly than does (**III**) and in NPhMe$_2$ at 150° gives (**I**) (23%) and 2 : 3 : 5 : 1-OH·$C_6H_2Cl_2$·CO_2H (13%). 2 : 4 : 1-$C_6H_3Cl_2$·O·CH_2·CH:CHMe [prep. from the phenol, (**II**), and K_2CO_3 in COMeEt], b.p. 90—103°/3 mm., rearranges more readily than does the allyl ether, b.p. 98—99°/2 mm. M.p. are corr. R. S. C.

Preparation and properties of *p*-thiolbenzoic acid. D. Bramley and N. H. Chamberlain (*J.C.S.*, 1942, 376).—A temp. of 90—100° is maintained during reduction (method: Smiles *et al.*, *J.C.S.*, 1922, **121**, 2024) of *p*-SO_2Cl·C_6H_4·CO_2H to give nearly pure *p*-SH·C_6H_4·CO_2H. A. T. P.

Alkyl carbonates. HI—V.—See A., 1942, II, 246.

Substituted succinic acids. I. R. H. Siddiqui and Salah-ud-din (*J. Indian Chem. Soc.*, 1941, **18**, 635—637).—*o*-C_6H_4Cl·CHO, CN·CH_2·CO_2·Et, and piperidine yield *o*-C_6H_4Cl·CH:C(CN)·CO_2Et, m.p. 225°, which with KCN in EtOH and hydrolysis with HCl gives *o*-chlorophenylsuccinic acid, m.p. 177° (anhydride, m.p. 119—120°; *monoanilide*, m.p. 168°). Similarly prepared, *Et α-cyano-β*-p- (**I**), m.p. 84°, and *-β*-o-*anisylacrylate* (**II**), m.p. 77°, give respectively *p*-, m.p. 206° and *o*-anisylsuccinic acid, m.p. 182°. CHPh:C(CN)·CO_2Et (**III**), m.p. 54°, was prepared similarly and converted into CO_2H·CHPh·CH_2·CO_2H. The *compounds*, m.p. 73°, 85°, and 69°, formed by addition of HCN to (**I**), (**II**), and (**III**), respectively, contain more N than is required for the CN·CHAr·CH(CN)·CO_2Et. F. R. G.

Alkyl*cyclo*pentanones. IV. Synthesis of α-1-carboxy-3-methyl-*cyclo*pentyl- and α-1-carboxy*cyclo*pentyl-β-phenylpropionic and α-1-carboxy*cyclo*pentylpropionic acids. R. D. Desai and G. S. Sahariya (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 93—96).—Successive treatments of CN·CHNa·CO_2Et suspended in EtOH with 3-methyl-*cyclo*pentanone cyanohydrin and CH_2PhCl give *Et α-cyano*-α-1-*cyano*-3-*methyl*cyclo*pentyl-β-phenylpropionate*, b.p. 252—254°/30 mm., hydrolysed by H_2SO_4 to α-1-*carboxy*-3-*methyl*cyclo*pentyl-β-phenylpropionic acid*, m.p. 112°, which gives a non-cryst. anhydride, sparingly sol. Pb and Cu salts, and freely sol. Ca and Ba salts. *cyclo*Pentanone cyanohydrin under similar conditions gives *Et α-cyano*-α-1-*cyano*cyclo*pentyl-β-phenylpropionate*, b.p. 220—225°/15 mm., m.p. 70°, hydrolysed (aq. H_2SO_4) to α-1-*carboxy*cyclo*pentyl-β-phenylpropionic acid*, m.p. 145° (*anhydride*, m.p. 115°; *anilic acid*, m.p. 159—160°). Et *cyclo*pentylidenecyanoacetate, CH_2PhCl, and NaOEt in hot EtOH yield *Et α-cyano*-α-Δ¹-cyclo*pentenyl-β-phenylpropionate*, b.p. 234—235°/16 mm., hydrolysed to α-Δ¹-cyclo*pentenyl-β-phenylpropionic acid*, m.p. 156—157°. Et sodio-1-cyano*cyclo*pentylcyanoacetate is methylated (MeI) to the *-α-cyanopropionate*, b.p. 152—154°/10 mm., hydrolysed to α-1-*carboxy*cyclo*pentylpropionic acid*, m.p. 140° (insol. Pb and sol. Cu, Ca, and Ba salts; non-cryst. anhydride; *anilic*, m.p. 170°, and p-*toluidinic acid*, m.p. 167°). H. W.

***cyclo*Hexane series. V. Isomeric α-1-carboxy-4- and -3-methyl-*cyclo*hexyl-β-phenylpropionic acids.** R. D. Desai, R. F. Hunter, and G. S. Sanariya (*Proc. Indian Acad. Sci.*, 1941, **14, A**, 516—520; cf. A., 1936, 1251; 1940, II, 130).—Successive treatments of CN·CHNa·CO_2Et in EtOH with 1-hydroxy-1-cyano-4-methyl*cyclo*hexane at room temp. and CH_2PhCl at room temp. and then at 100° yield *Et α-cyano*-α-1-*cyano*-4-*methyl*cyclo*hexyl-β-phenylpropionate* (**I**), b.p. 230—234°/6 mm., m.p. 84—92°, and some α-1-*cyano*-4-*methyl*cyclo*hexyl-β-phenylpropionitrile* (**II**), m.p. 143°. (**I**) is hydrolysed by H_2SO_4 to a mixture of α-1-*carboxy*-4-*methyl*cyclo*hexyl-β-phenylpropionic acids* (*A*), m.p. 183° (decomp.) [*anhydride*, m.p. 115°; *anilic acid* (+0·5H_2O), m.p. 165° *imide*, m.p. 181°], and (*B*), m.p. 195° [also obtained from (**II**)] [*anhydride*, m.p. 109°; *anilic acid* (+0·5H_2O), m.p. 175°]. Similarly, *Et α-cyano*-α-1-*cyano*-3-*methyl*-cyclo*hexyl-β-phenylpropionate*, b.p. 237—239°/8 mm., m.p. 95—105°, is hydrolysed to a mixture of α-1-*carboxy*-3-*methyl*cyclo*hexyl-β-phenylpropionic acids* (*C*), m.p. 184° (*anhydride*, m.p. 102°; *anilic acid*, m.p. 152°; *imide*, m.p. 165—166°), and (*D*), m.p. 178° (*anhydride*, m.p. 130°, *anilic acid*, m.p. 170°). The results can be interpreted on the uniplanar form of the *cyclo*hexane ring. H. W.

Diethyl 1 : 4-dihydroxy-2 : 3-naphthalate. A. H. Homeyer and V. H. Wallingford (*J. Amer. Chem. Soc.*, 1942, **64**, 798—801).—1 : 4 : 2 : 3-$(OH)_2C_{10}H_4(CO_2Et)_2$ (**I**) [prep. from *o*-$C_6H_4(CO_2Et)_2$, $(CH_2·CO_2Et)_2$, and NaOEt in 48% yield] with MeI–NaOEt–EtOH gives *Et*$_2$ 1-*hydroxy*-4-*methoxy*- (**II**), m.p. 80—81°, and then or directly [with some impure Et_2 2 : 3-dimethyl-2 : 3-dihydro-1 : 4-naphthaquinone-2 : 3-dicarboxylate (*A*), b.p. 175—180°/3 mm., hydrolysed (EtOH–NaOH–N_2) to 2 : 3 : 1 : 4-$C_{10}H_4Me_2(OH)_2$] *Et*$_2$ 1 : 4-*dimethoxy-naphthalene*-2 : 3-*dicarboxylate* (**III**), m.p. 48—49°. In warm NaOH–EtOH–H_2O, (**III**) gives 1 : 4-*dimethoxynaphthalene*-2 : 3-*dicarboxylic acid*, which at < 120° loses H_2O to give the *anhydride*, m.p. 203—204°. When boiled in aq. NaOH and then kept at 70°, (**II**) gives 4-*hydroxy*-1-*methoxy*-2-*naphthoic acid*, m.p. 217—218°, converted by CH_2N_2 (4 mols.) in MeOH–Et_2O into *Me* 1 : 4-*dimethoxy*-2-*naphthoate* (**IV**), m.p. 57—59°. When kept in aq. NaOH containing a little $Na_2S_2O_4$, (**I**) loses CO_2 and gives 1 : 4 : 2-$(OH)_2C_{10}H_5$·CO_2H, m.p. ~200° (decomp.) (lit. 186°) [with Ac_2O–NaOAc yields 1 : 5-$C_{10}H_6(OAc)_2$]. In boiling HCl–MeOH this gives 1 : 4 : 2-OH·$C_{10}H_5$(OMe)·CO_2H (**V**), m.p. 196—198° (decomp.) (lit. 178°, 180°), and -OH·$C_{10}H_5$(OMe)·CO_2Me (**VI**), m.p. 137—138° (lit. 134°). CH_2N_2 (4 mols.) in MeOH–Et_2O converts (**V**) into (**VI**), but MeI–NaOMe or a large excess of CH_2N_2 gives some (**IV**). The vitamin-*K* activity of (*A*) approx. equals that of 2-methyl-1 : 4-naphthaquinone; the other products are inactive. R. S. C.

Chemistry and biochemistry of plant substances. VIII. Galloylellagic acid. L. Reichel and A. Schwab (*Annalen*, 1942, **550**, 152—159).—Ellagic acid (in aq. NaOH and H_2) shaken with tricarbomethoxygalloyl chloride in cold $COMe_2$ gives *tetra(tricarbomethoxygalloyl)ellagic acid*, m.p. 182—185°, converted (N-NH_3 at room temp. in H_2, then aq. H_2SO_4) into *tetragalloylellagic acid* (+11H_2O), decomp. ~300—320°. Tetracarbethoxyellagic acid, new m.p. 247°, and boiling aq. NaOH–dioxan (5 min.) give the *Na*$_2$ salt and thence (warm 2N-H_2SO_4) *dicarbethoxyellagic acid*, decomp. 350—380°, *dicarbethoxybis(tricarbomethoxygalloyl)ellagic acid*, m.p. 106—110°, and *digalloylellagic acid* (+7H_2O), decomp. 300—310°. A. T. P.

Preparation of 4-nitrosalicylaldehyde. J. R. Segesser and M. Calvin (*J. Amer. Chem. Soc.*, 1942, **64**, 825—826).—Addition of Br to an illuminated (W lamp) solution of 4 : 1 : 2-NO_2·C_6H_3Me·OAc in CCl_4 gives successively *4-nitro*-2-*acetoxy-benzyl bromide*, m.p. 82°, and *-benzylidene dibromide* (**I**), m.p. 77—78°. In conc. H_2SO_4 at 50° and then 100°, (**I**) gives *4-nitrosalicylaldehyde* (**II**), m.p. 133—134° (2 : 4-dinitrophenyl-, decomp. ~323°, and phenyl-hydrazone, m.p. 168—169°). *m*-NO_2·C_6H_4·OH with NPhMe·CHO–$POCl_3$ gives a H_2O-sol. green compound and by the Reimer–Tiemann reaction a little $CH(O·C_6H_4·NO_2-m)_3$ which cannot be rearranged. R. S. C.

Synthesis of compounds related to mould metabolic products. I. 3 : 5-Dihydroxy-2-formylbenzoic acid and 3 : 5-dihydroxyphthalic acid. J. H. Birkinshaw and A. Bracken (*J.C.S.*, 1942, 368—370).—3 : 5 : 1-$(SO_3K)_2C_6H_3$·CO_2H and KOH at 360° afford 3 : 5 : 1-$(OH)_2C_6H_3$·CO_2H. 3 : 5 : 1-$(OH)_2C_6H_3$·CO_2Me and $Zn(CN)_2$–$AlCl_3$–HCl–Et_2O give *Me* 3 : 5-*dihydroxy*-2-*formylbenzoate* (**I**), m.p. 163·5° [2 : 4-*dinitrophenylhydrazone*, m.p. 293° (decomp.) or 297° (decomp.) (pre-heated to 288°)], hydrolysed [15% aq. NaOH at room temp. (3 days)] to the *acid*, m.p. 233° (decomp.) [2 : 4-*dinitrophenylhydrazone*, m.p. 301° (decomp.)]. KOH and (**I**) at 180—190° give 3 : 5 : 1 : 2-$(OH)_2C_6H_2(CO_2H)_2$. A. T. P.

Dialdehydes of phloroglucinol and its homologues. W. Gruber (*Ber.*, 1942, **75**, [*B*], 29—33).—Treatment of 1 : 3 : 5-$C_6H_3(OH)_3$ with $Zn(CN)_2$ and HCl in abs. Et_2O and of the product with saturated aq. $NaHCO_3$ gives *phloroglucinoldialdehyde* (1·5% yield), m.p. 221—224° (vac.; decomp.), identified by reduction (Clemmensen) to 2 : 4 : 1 : 3 : 5-$C_6HMe_2(OH)_3$, m.p. 160—161°. 2 : 1 : 3 : 5-$C_6H_2Me_2(OH)_2$, anhyd. HCN, and HCl in abs. Et_2O yield an aldimide mixture, hydrolysed by $NaHCO_3$ which removes C-*methylphloroglucinoldialdehyde*, m.p. 225—227° (vac.; decomp.) when rapidly heated [*bisphenylhydrazone*, m.p. 230—232° (vac.; decomp.)], reduced to *trimethylphloroglucinol*, m.p. 187—189°. The use is described of anhyd. HCN in the prep. of C-*ethylphloroglucinoldialdehyde*, m.p. 176—178° (vac.; decomp.) [*bisphenylhydrazone*, m.p. 230—232° (vac.; decomp.); reduced to *dimethylethylphloroglucinol*, m.p. 135—136°], and iso*amylphloroglucinoldialdehyde*, m.p. 176—177° (reduced to *dimethyl*iso*amylphloroglucinol*), and, mainly, the non-cryst. monoaldehyde [*phenylhydrazone*, m.p. 204—206° (decomp.; vac.)]. H. W.

Action of an aluminium–aluminium chloride catalyst in Friedel–Crafts reactions. Benzoylation. O. Grummitt and E. N. Case (*J. Amer. Chem. Soc.*, 1942, **64**, 878—880).—1 : 0·55 : 0·57 (mol.) C_6H_6–BzCl–$AlCl_3$ in CS_2 give 62% of $COPh_2$, also if Al (0·54) is added. Reactants in the ratio 1 : 0·179 : 0·182 (no solvent) give 90% of $COPh_2$, greatly reduced (46, 18, and 9% at 25—30°, 50°, and 80°, respectively) by presence of Al which leads also to C_2Ph_4, *p*-COPh·C_6H_4·$CHPh_2$, and resins. These products are formed by reduction (Al + HCl → H_2) of $COPh_2$ to $(CPh_2·OH)_2$ and decomp thereof by way of epoxytetraphenylethane and CPh_3·COPh. Thi. mechanism is confirmed by (i) evolution of H_2 during the Al–AlCs reaction, (ii) stability of $COPh_2$ to Al–$AlCl_3$, and (iii) formation l$_3$ similar products from $COPh_2$ by Al–$AlCl_3$–HCl. R. S. C.of

Effects of water on the photochemical bromination of acetophenone.—See A., 1942, I, 273.

Synthesis of potential cortical hormone substitutes. Hydroxycarbonyl derivatives of diphenyl ether and related compounds. J. Walker (*J.C.S.*, 1942, 347—353).—*p*-C_6H_4Br·OMe (**I**), *p*-OH·C_6H_4·CO_2Et, K_2CO_3, and Cu-bronze at 200—215° yield (after hydrolysis with aq. KOH) *p*-OMe·C_6H_4·O·C_6H_4·CO_2H-*p* (**II**), m.p. 176—177°, converted by boiling HBr–AcOH into 4-4′-*hydroxyphenoxybenzoic acid*, m.p. 192—193° (*Et* ester, m.p. 112—113°), and thence (Ac_2O–N-NaOH at 0°) into the 4′-*OAc-acid* (**III**), m.p. 149—150°. $SOCl_2$–$CHCl_3$ and (**III**) give the chloride, which with CH_2N_2–Et_2O at room temp. yields *ω-diazo*-4-(4′-*acetoxyphenoxy*)*acetophenone* (**IV**), m.p. 118—119·5°, and thence (AcOH) the *ω-OAc*-compound (**V**), m.p. 117·5—118°. (**IV**) and 2N-H_2SO_4–dioxan at

50°, then N-HCl–EtOH, give *ω-hydroxy-4-(4′-hydroxyphenoxy)-acetophenone*, m.p. 171—172·5°, also obtained from (V) with aq. EtOH–HCl. 3 : 4 : 1-OMe·C_6H_3(ONa)·CO_2Et, (I), and Cu-bronze–Cu(OAc)$_2$ at 240°, then MeOH–KOH, yield 4-(4′-*methoxyphenoxy*)-3-*methoxybenzoic acid*, m.p. 170—171°, and thence (AcOH–HBr) 3-*hydroxy*-4-(4′-*hydroxyphenoxy*)*benzoic acid*, m.p. 204—205° (*Et* ester, m.p. 128—129°). The corresponding 3 : 4-(*OAc*)$_2$-*acid* (VI), m.p. 173—174°, gives *ω* : 3-*diacetoxy*-4-(4′-*acetoxyphenoxy*)*acetophenone*, b.p. ~255°/1·6 mm., converted by Cu(OAc)$_2$–CH_2O–aq.NH_3, followed by picric acid, into the *picrate* (+1·5H_2O), effervesces at 128—130°, resolidifies and melts at 183—184°, of 2 : 4′-dihydroxy-4-4″-iminazolyldiphenyl ether. The chloride of (III) and CHNaAc·CO_2Et–C_6H_6 (reflux, then room temp.) give a Na derivative, converted by aq. NH_3–NH_4Cl into the intermediate *β*-keto-ester (*phenylpyrazolone*, m.p. 128·5—130°) and thence (10% aq. H_2SO_4) 4-(4′-*hydroxyphenoxy*)*acetophenone*, (VII), m.p. 155—156°. The chloride of (VI) similarly yields 3-*hydroxy*-4-(4′-*hydroxyphenoxy*)-*acetophenone* (VIII), m.p. 149—150·5° (2 : 4-*dinitrophenylhydrazone*, m.p. 234°). *p*-OMe·C_6H_4·OPh (IX) and AcCl–$AlCl_3$–CS_2 at room temp. afford 4-(4′-*methoxyphenoxy*)*acetophenone*, m.p. 60—61° (2 : 4-*dinitrophenylhydrazone*, m.p. 171°) [also obtained from (VII) and aq. Me_2SO_4–KOH], oxidised (NaOCl) to (II). 2 : 5 : 1-OMe·C_6H_3Br·CO_2Et and NaOPh–Cu-bronze–Cu(OAc)$_2$ at 230° afford *Et* 5-*phenoxy*-2-*methoxybenzoate*, m.p. 63° (free *acid*, m.p. 108·5—110°). 4-(4′-Methoxyphenoxy)cinnamic acid, new m.p. 176—177° (*Me* ester, m.p. 129—130°), is hydrogenated (Pd–$SrCO_3$–EtOAc) to *Me* *β*-4-(4′-*methoxyphenoxy*)*phenylpropionate*, m.p. 55—56°, converted by boiling HBr–AcOH into *β*-4-(4′-*hydroxyphenoxy*)*phenylpropionic acid*, m.p. 161° (*Et* ester, m.p. 76—77°). NPhMe·CHO, (IX), and $POCl_2$ at 100° (bath) give only a little *p*-OMe·C_6H_4·O·C_6H_4·CHO-*p* (semicarbazone, new m.p. 215°). (V), (VII), and (VIII) show no progesterone activity. A. T. P.

Condensation of succinic anhydride with resorcinol and orcinol. Further case of γ-substitution in orcinol. R. D. Desai and (Mrs.) V. H. Shroff (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 97—98).—*m*-$C_6H_4(OH)_2$ is converted by $AlCl_3$ and $(CH_2{\cdot}CO)_2O$ (I) in $PhNO_2$ at room temp. and then at 100° into *β*-2 : 4-*dihydroxybenzoylpropionic acid*, m.p. 199—200° [p-*nitrophenylhydrazone*, m.p. 194° (decomp.)], oxidised by NaOBr to *β*-resorcylic acid. Similarly orcinol affords *β*-3 : 5-*dihydroxy*-p-*toluoylpropionic acid*, m.p. 207° [p-*nitrophenylhydrazone*, m.p. 203—204° (decomp.)], oxidised to *p*-orsellinic acid. Resacetophenone, (II), 1 : 3 : 5-$C_6H_3(OH)_3$, Me *β*-resorcylate (III), and *α*-$C_{10}H_7$·OH could not be condensed with (I) in presence of anhyd. $AlCl_3$ or $ZnCl_2$ in $PhNO_2$ or $C_2H_2Cl_4$. (II) or (III) does not condense with $CO_2Et{\cdot}[CH_2]_2{\cdot}COCl$ in presence of $AlCl_3$ or $ZnCl_2$. H. W.

Action of benzoyl chloride on ethyl β-diethylaminocrotonate. W. M. Lauer and N. H. Cromwell (*J. Amer. Chem. Soc.*, 1942, **64**, 612—614).—NEt_2·CMe:CH·CO_2Et and BzCl in Et_2O at 0° give mixed hydrochlorides, whence are obtained by hydrolysis in H_2O at room temp. *Et* *β-diethylamino-αγ-dibenzoylcrotonate* [*β-diethylamino-δ-hydroxy-α-benzoyl-δ-phenyl-*$\Delta^{\alpha\gamma}$*-pentadienoate*] (I), m.p. 76·5—77·5° (*hydrochloride*, m.p. 125—126°, obtained by HCl–Et_2O), and, by treatment of the filtrate with aq. NH_3 (?) *Et* *δ-amino-β-diethylamino-benzoyl-δ-phenyl-*$\Delta^{\alpha\gamma}$*-pentadienoate*, m.p. 129—131°. In boiling 1·4% H_2SO_4 or AcOH, (I) gives 4-*diethylamino*-3-*benzoyl*-6-*phenyl*-2-*pyrone* (II), m.p. 126—127°, also obtained by treating dehydrobenzoylacetic acid (III) successively with PCl_5–$POCl_3$ and $NHEt_2$. In 15% aq. NaOH, (I) gives a Na salt, but in 1% NaOH gives slowly (II) and some BzOH. NPr^n_2·CMe:CH·CO_2Et and BzCl–Et_2O give *Et* *β-di*-n-*propylamino-αγ-dibenzoylcrotonate*, m.p. 71—72°, hydrolysed by boiling AcOH to 4-*di*-n-*propylamino*-3-*benzoyl*-6-*phenyl*-2-*pyrone*, m.p. 147—147·5°, also obtained (cf. above) from (III). R. S. C.

Condensation of maleic anhydride with naphthyl methyl ethers. K. P. Dave, K. U. Bokil, and K. S. Nargund (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 122—123).—Condensation of *α*-$C_{10}H_7$·OMe with $(CH{\cdot}CO)_2O$ (I) in $PhNO_2$ gives an 88% yield of *β*-4-*methoxy*-1-*naphthoylacrylic acid*, m.p. 192—193° (resinous Me and Et ester; *dibromide*, m.p. 160°), oxidised ($KMnO_4$) to 4 : 1-OMe·$C_{10}H_5$·CO_2H, m.p. 230°. Under similar conditions *β*-$C_{10}H_7$·OMe and (I) give a product, m.p. 105—120°, consisting mainly of 2-methoxy-1-naphthoylacrylic acid since it gives a large proportion of 2 : 1-OMe·$C_{10}H_5$·CO_2H when oxidised. H. W.

Conjugated systems. XVI. Condensation of dienes with unsaturated aryl ketones. N. A. Naschtschinskaja and A. A. Petrov (*J. Gen. Chem. Russ.*, 1941, **11**, 665—668).—$(CH_2{:}CH)_2$ (I) and CHPh:CH·COMe at 170—180° for 10 hr. give 2-*acetyl*-1-*phenyl*-Δ^4-cyclo*hexene* (47% yield), m.p. 62·2—62·7° (*oxime*, m.p. 94·5—95°; semicarbazone, m.p. 175—175°). (I) and CHPh:CH·COPh (II) afford 2-*benzoyl*-1-*phenyl*-Δ^4-cyclo*hexene* (82% yield), m.p. 100·4—101·5° (*dibromide*, m.p. 120·2—121·2°). (I) and $CO(CH{:}CHPh)_2$ give 2 : 2′-*diphenyl*-$\Delta^{4:4'}$-*octahydrobenzophenone*, m.p. 163·5—164·7° (*tetrabromide*, m.p. 235—236°). Isoprene and (II) give 2-*benzoyl*-1-*phenyl*-5-*methyl*-Δ^4-cyclo*hexene* (56·6% yield) (*dibromide*, m.p. 111·5—112°, and a higher bromide, m.p. 153—154·5°). G. A. R. K.

Conjugated systems. XV. Condensation of alkoxybutadienes with acraldehyde. Synthesis of 4-ketohexahydrobenzaldehyde and derivatives. A. A. Petrov (*J. Gen. Chem. Russ.*, 1941, **11**, 661—664).—*β*-Methoxybutadiene and $CH_2{:}CH{\cdot}CHO$ (containing 0·7% of quinol) at 120—140° for 6 hr. give 65% of 4-*methoxy*-Δ^3-*tetrahydrobenzaldehyde* (I), b.p. 92—92·5°/10 mm.; *β*-ethoxybutadiene similarly affords (50%) 4-*ethoxy*-Δ^3-*tetrahydrobenzaldehyde*, b.p. 101·5—102°/10 mm. (I) is partly polymerised on keeping for a year; the remainder undergoes hydrolysis by atm. H_2O to 4-*ketohexahydrobenzaldehyde* (II), b.p. 113—113·5°/10 mm., also rapidly produced on shaking (I) with dil. H_2SO_4; it is miscible with H_2O, not volatile in steam, and polymerises to a solid on keeping (disemicarbazone, m.p. 199°; *p*-nitrophenylhydrazone). (II) is oxidised by $KMnO_4$ to 4-keto*cyclo*hexane-1-carboxylic acid. G. A. R. K.

Reactions of perinaphthane derivatives. L. F. Fieser and L. W. Newton (*J. Amer. Chem. Soc.*, 1942, **64**, 917—921).—Perinaphthen-7-one (I) (A., 1938, II, 356) with $Na_2S_2O_4$ gives a red vat, with NH_2OH,HCl in abs. EtOH gives an *oxime*, sinters at 165°, m.p. 166·8—167·3° (cf. lit.), and with $NaHSO_3$ in aq. EtOH and then NH_2Ph gives the *salt*, $C_{10}H_6\langle^{CH(SO_3H,NH_2Ph)}_{CO}\rangle CH_2$, m.p. 173·2—174·6° (decomp.), which regenerates (I) in boiling, dil. HCl. (I) does not undergo the Michael, Diels–Alder, or Friedel–Crafts (C_6H_6–$AlCl_3$) reaction, but with BzCl–$AlCl_3$–$ZnCl_2$ at 130—140° gives 8-*benzoylperinaphthen*-7-*one* (II) (>38%), m.p. 167·9—168·4° (red vat; proof of structure by synthesis below), and small amounts of an *isomeride*, m.p. 304—307°, and a *substance*, m.p. 274—275° (decomp.). Perinaphthan-7-ol is best (80%) obtained by hydrogenation of (I) in presence of old Raney Ni, but fresh catalyst gives also much phenol; dehydration by Tschugaev's method or by PCl_5–$POCl_3$ and later C_5H_5N failed. With MgMeI–Et_2O and later aq. NH_4Cl, (I) gives 7-*methylperinaphthan*-7-*ol* (67%), m.p. 74·6—76·1°, dehydrated by boiling HCl–abs. EtOH to 7-*methylperinaphthene*, m.p. 59·5—60·3° [purified by Al_2O_3; picrate, m.p. 174·5° (decomp.)], stable in N_2 (becomes green) but not in air. (I) is more stable than is 1 : 2 : 4-O:$C_{10}H_5$Me:O to H_2O_2–Na_2CO_3–EtOH–H_2O, but after rather long boiling gives 8 : 9-*epoxyperinaphthan*-7-*one* (58%), sinters at 116°, m.p. 117—117·4°, which in conc. H_2SO_4 gives 8-*hydroxyperinaphthen*-7-*one* [*perinaphthane*-7 : 8-*dione*] (III) (98·5%), m.p. 184·4—185° (*acetate*, m.p. 183·5—185·5°; *benzoate*, sinters at 159°, m.p. 163·5—165·6°). Br–AcOH at 100° converts (I) into the 8-*Br*-derivative, m.p. 152—152·4°, which could not be converted into (III). Perinaphthen-7-one-8-carboxylic acid (IV) (prep. from 2 : 3-OH·$C_{10}H_6$·CO_2H, glycerol, NO_2·C_6H_4·SO_3Na, H_2SO_4, and H_2O modified; 18·7% yield), sinters at 275°, m.p. 284·5—285° (gas), when heated at 3—5 mm. gives (I) and with PCl_5–C_6H_6 gives the acid *chloride*, sinters at 207°, m.p. 209—211°, which with C_6H_6–$AlCl_3$ yields (II) (40%). $(CH_2{:}CMe)_2$ and (IV) in boiling AcOH give 9 : 10-*dimethyl*-(? 8 : 11-)*di*- (V), m.p. 188·6—189·4°, and -7*a* : 8 : 11 : 11*a*-*tetra-hydrobenzanthr*-7-*one*, m.p. 124·7—125·2°, or after prolonged boiling 9 : 10-*dimethylbenzanthr*-7-*one*, m.p. 188·6—189·4°, also obtained from (V) by Pd–C at 300° and oxidised by CrO_3–AcOH to 2 : 3-*dimethylanthraquinone*-5-*carboxylic acid*, m.p. 313—314° (decomp. from ~310°; uncorr.) [*compound* with Ac_2O, m.p. 215—217° (loss of solvent), resolidifies, remelts at 312—316° (uncorr.)], which with Cu-bronze in quinoline at 170° gives 2 : 3-dimethylanthraquinone. M.p. are corr. R. S. C.

Preparation of 2-iodo-*p*-benzoquinone. H. H. Hodgson and D. E. Nicholson (*J.C.S.*, 1942, 375—376).—1 : 3 : 4-OH·C_6H_2I·NH_2 and aq. $Fe_2(SO_4)_3$ give 2-*iodo*-p-*benzoquinone*, m.p. 62°. A. T. P.

Sulphonation. VII. Sulphonation of 1 : 2-benzanthraquinone with sulphuric acid. J. S. Joffe and N. M. Fedorova (*J. Gen. Chem. Russ.*, 1941, **11**, 619—625).—1 : 2-Benzanthraquinone with 96% H_2SO_4 at 150—160° for 5—6 hr. affords 1 : 2-*benzanthraquinone*-2′-*sulphonic acid* (I), isolated as the K salt (80% yield), apparently the sole product formed (cf. Sempronj, A., 1939, II, 514). Mild fusion of (I) with KOH gives 2′-*hydroxy*-1 : 2-*benzanthraquinone* (II), m.p. 248—250° [*acetate* (III), m.p. 253—255°], forming blue solutions in alkali. A by-product is 2 : 7-OH·$C_{10}H_6$·CO_2H, m.p. 268—269° (acetate, m.p. 209°), also formed when (I) or (II) is fused with KOH under drastic conditions [when no 2 : 8-OH·$C_{10}H_6$·CO_2H is formed, so that fission always takes place between CO and the *α*- and not the *β*-C atom (cf. *loc. cit.*)]. Reduction of (I) with Zn dust and aq. NH_3 gives 1 : 2-*benzanthracene*-2′-*sulphonic acid*, forming 2′-*hydroxy*-1 : 2-*benzanthracene* (IV), m.p. 178—179° [*acetate* (V), m.p. 152—153°], on alkaline fusion. (IV) couples with ArN_2Cl to form azo-dyes (*e.g.*, dye, m.p. 248—249°, with 2 : 4 : 1-$C_6H_3Cl_2$·N_2Cl). (V) is oxidised (CrO_3) to (III). G. A. R. K.

Perylene and its derivatives. LV. Supposed 1 : 12-furano-2 : 3 : 10 : 11-dibenzoperylene-4 : 9-quinone of E. Clar. A. Zinke, E. Ziegler, and H. Gottschall [with, in part, K. Lercher] (*Ber.*, 1942, **75**, [*B*], 148—151).—The alkali-insol. product obtained by Clar (A., 1932, 731) by the oxidation of his dibenzoperylene is 2 : 3 : 8 : 9-*dibenzoperylene*-4 : 10-*quinone* (I), m.p. 367° after becoming discoloured at 360°. It is converted (aq. NaOH–$Na_2S_2O_4$, then Et_2O–*p*-C_6H_4Br·COCl) into 4 : 10-*di*-p-*bromobenzoyloxy*-2 : 3 : 8 : 9-*dibenzoperylene*, m.p. 344°, and chlorinated by Cl_2 in dry $PhNO_2$ at 100° to a *substance*, $C_{28}H_{12}O_2Cl_6$, decomp. ~300° after darkening at 220°, converted by boiling $PhNO_2$–C_5H_5N into the *compound*, $C_{28}H_{10}O_2Cl_4$,

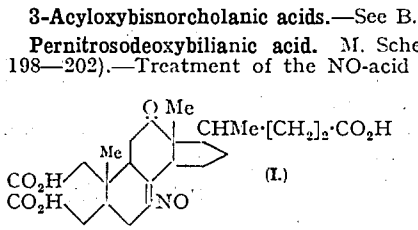
m.p. >350°. (I) is oxidised by CrO_3 in boiling AcOH to (?) an *acid*, $C_{27}H_{14}O_5$, m.p. 300—302°. H. W.

IV.—STEROLS AND STEROID SAPOGENINS.

sym.-**Dicholesteryl pyrophosphate dihydrate.** T. Wagner-Jauregg and T. Lennartz (*Ber.*, 1942, **75**, [*B*], 178—179).—Dicholesteryl H_2 pyrophosphate dihydrate (**I**) is converted by K in boiling PhMe into the K_1 salt, m.p. 186—189° (darkens at 180°). The Na_4 salt and boiling AcOH yield the Na_1 salt, m.p. 178—180°. (**I**) contains 4 active H (Zerevitinov). H. W.

3-Acyloxybisnorcholanic acids.—See B., 1942, III, 171.

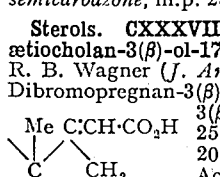
Pernitrosodeoxybilianic acid. M. Schenck (*Ber.*, 1942, **75**, [*B*], 198—202).—Treatment of the NO-acid (**I**) with 23% aq. $NaNO_2$ in AcOH gives the enol-nitrate, $C_{24}H_{33}O_{10}N$, decomp. 125°, also obtained from *iso*bilianic acid dioxime. Deoxybilianic acid oxime and HNO_2 afford the *pernitroso-acid*, $C_{24}H_{30}O_8N_2$, decomp. 110°, which does not give a colour with $NHPh_2$–H_2SO_4. It evolves N_2O when treated with conc. H_2SO_4 or, particularly easily, with NaOH. H. W.


(I.)

Total synthesis of a stereoisomeride of the sex hormone, œstrone. W. E. Bachmann, S. Kushner, and A. C. Stevenson (*J. Amer. Chem. Soc.*, 1942, **64**, 974—981).—$[CH_2]_3(CO)_2O$ [prep. from $CO_2Me{\cdot}[CH_2]_2{\cdot}CH(CO_2Et)_2$ by boiling 18% HCl and later AcCl], m.p. 52—55°, b.p. 165—170°/20 mm., with EtOH gives the Et H ester and thence $(SOCl_2)$ $CO_2Et{\cdot}[CH_2]_3{\cdot}COCl$, which with *m*-$OMe{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}CH(CO_2Et)_2$ (modified prep.), b.p. 195—200°/0·6—0·8 mm., in C_6H_6 at, first, room temp. and then the b.p. gives Et δ-keto-εε-dicarbethoxy-η-*m*-anisyl-*n*-octoate (52%), b.p. 210—220°/0·05 mm., converted by 100% H_3PO_4 at 42° and then KOH–MeOH–H_2O into γ-2 : 2-*dicarboxy*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylidene*-n-*butyric acid* (**I**), m.p. 180·5—182° (gas; bath preheated at 175°). This is decarboxylated and rearranged in boiling H_2O to γ-2-*carboxy*-6-*methoxy*-3 : 4-*dihydro*-1-*naphthyl*-n-*butyric acid* (**II**) (52%), m.p. 189—190° (decomp.), the structure of which is proved by conversion by boiling HCl–AcOH–H_2O–N_2 or of its Me_2 ester (**III**) (prep. by CH_2N_2) by NaOMe–C_6H_6–N_2 into 1-keto-7-methoxy-1 : 2 : 3 : 4 : 9 : 10-hexahydrophenanthrene (**IV**), m.p. 76—77·5°, also obtained similarly (both methods) from (**I**) and from *m*-$OMe{\cdot}C_6H_4{\cdot}[CH_2]_3{\cdot}CO{\cdot}[CH_2]_3{\cdot}CO_2Me$ by boiling NaOMe–C_6H_6 (gives 2-β-*m*-anisylethyl*cyclo*hexane-1 : 3-dione, m.p. 150—152°) and then H_3PO_4 at 100° (cf. Robinson *et al.*, A., 1935, 1499; Hewett, A., 1936, 326). Ring-closure of (**III**) and methylation (MeI–MeOH–C_6H_6) of the crude Na derivative gives *Me* 1-*keto*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4 : 9 : 10-*hexahydrophenanthrene*-2-*carboxylate* (**V**), m.p. 98—100°, which affords (Reformatsky) *Me* 1-*hydroxy*-2-*carbomethoxy*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4 : 9 : 10-*hexahydro*-1-*phenanthrylacetate* (**VI**) (69%), m.p. 112—113°, converted by hot KOH–MeOH–H_2O into the known (*loc. cit.*) 2-Me derivative of (**IV**) [also obtained similarly from (**V**)]. With dry HCl–C_6H_6 at 15° or warm HCO_2H–C_6H_6, (**VI**) gives *Me* 2-*carbomethoxy*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4 : 9 : 10-*hexahydro*-1-*phenanthrylideneacetate*, m.p. 136·5—138°, isomerised by Pd–C at 300° to the known Me 1 : 2 : 3 : 4-tetrahydro-1-phenanthrylacetate and hydrogenated (Pd–C; EtOH) to mixed stereoisomeric 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-H_8-esters. Half hydrolysis (NaOH–MeOH–H_2O–N_2), lengthening of the chain (Arndt–Eistert), ring-closure (NaOMe–C_6H_6–N_2) to mixed 16-carbomethoxyœstrone Me ethers, hydrolysis and decarboxylation (HCl–AcOH–H_2O–N_2) to mixed œstrone Me ethers (distilled at 180°/0·05 mm.), and finally demethylation (48% aq. HBr–AcOH) gives mixed œstrones (**VII**), solid. In MeOH these deposit *œstrone*-a (**VIII**), m.p. 214—214·5°, sublimes at 200°/0·05 mm. (*benzoate*, m.p. 175—176° after slight softening), the Na salt of which with Me_2SO_4 in H_2O gives the Me ether, dimorphic, m.p. 81·5—82° and 101·5—102·5°, converted by, successively, MgMeI, $KHSO_4$, and Pd–C at 300° into 7-methoxy-3′ : 3′-dimethyl-1 : 2-*cyclo*pentanophenanthrene, m.p. 162—163·5°, identical with that obtained from equilenin Me ether. Hydrogenation (Pd–C; AcOH) of (**II**) gives γ-2-*carboxy*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthyl*-n-*butyric acid*, m.p. 156—157·5°, the Me_2 ester of which, when cyclised as above and then boiled in HCl–AcOH–H_2O–N_2, gives the known 1-keto-7-methoxy-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene (**IX**), m.p. 107—108°, or, when cyclised and then methylated as above, yields the oily 2-carbomethoxy-2-methyl and thence (KOH–MeOH–H_2O) the 2-Me derivative of (**IX**). Reduction of (**II**) by 2% Na–Hg in H_2O gives an acid, whence cyclisation etc. gives mixed ketones including some (**IX**). The absorption spectrum of (**VIII**) very closely resembles that of œstrone (**X**). Doses of (**X**), (**VII**), and (**VIII**) for equal œstrogenic activity are 1 : 50 : 250. (**VIII**) is a *dl*-form of a stereoisomeride of (**X**). R. S. C.

Sterols. CXL. 17-Bromo- and 17 : 21-dibromo-*allo*pregnan-20-one. R. E. Marker, H. M. Crooks, jun., R. B. Wagner, A. C. Shabica, E. M. Jones, and E. L. Wittbecker (*J. Amer. Chem. Soc.*, 1942, **64**, 822—824).—*allo*Pregnan-20-one (**I**) with Br in AcOH + a little HBr at room temp. gives 17-*bromo*- (**II**), m.p. 127—129°, and then at 40° 17 : 21-*dibromo*-allo*pregnan*-20-*one* (**III**), m.p. 128—130°. (**I**) is regenerated from (**II**) by Zn powder or Fe filings in AcOH at 100° or by H_2–Pd–$BaSO_4$–C_5H_5N–MeOH at 2 atm., and from (**III**) by Zn– or Fe–AcOH or HCO_2H–HCO_2K at 130°. In boiling C_5H_5N, (**II**) gives Δ^{16}-allo*pregnen*-20-*one*, m.p. 156—158°, hydrogenated (Pd–$BaSO_4$) in EtOH–dioxan to (**I**). With hot KOH–MeOH, (**III**) gives $\Delta^{17:20}$-allo*pregnenoic* 21-*acid*, m.g. 242—244°, converted by O_3 into $CHCl_3$ into *androstan*-17-*one*, m.p. 117—119°, isolated as *semicarbazone*, m.p. 284—285° (decomp.). R. S. C.

Sterols. CXXXVIII. Conversion of pregnan-3(β)-ol-20-one into ætiocholan-3(β)-ol-17-one. R. E. Marker, H. M. Crooks, jun., and R. B. Wagner (*J. Amer. Chem. Soc.*, 1942, **64**, 817—818).—17 : 21-Dibromopregnan-3(β)-ol-20-one in boiling KOH–MeOH–H_2O gives 3(β)-*hydroxy*-$\Delta^{17:20}$-*pregnenoic* 21-*acid* (**I**), m.p. 257—258° (decomp.) [*acetate* (**II**), +H_2O, m.p. 209—212°, and (?) its mixed *anhydride* with AcOH, m.p. 234°], reduced by H_2–PtO_2 in AcOH at 3 atm. to 3(β)-*hydroxypregnanoic* 21-*acid*, m.p. 219—221°. (**II**) with O_3–$CHCl_3$ or CrO_3–AcOH at 50—55° gives (after hydrolysis) ætiocholan-3(β)-ol-17-one (isolated as semicarbazone and obtained therefrom by boiling H_2SO_4–H_2O–EtOH). R. S. C.


(I.)

Separation of pregnenolone esters.—See B., 1942, III, 172.

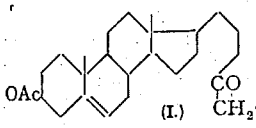
Constituents of the adrenal cortex and related substances. LV. *allo*Pregnane-3(β) : 17(α) : 21-triol-20-one and attempts to prepare other 17(α)-hydroxypregnane derivatives with dihydroxyacetone grouping. D. A. Prins and T. Reichstein (*Helv. Chim. Acta*, 1942, **25**, 300—322).—Δ^{20}-*allo*Pregnene-3(β) : 17(α)-diol diacetate and Et_2O–OsO_4 give a mixture of Os esters, converted by agitation with aq. $HClO_3$ in Et_2O into a difficultly separable mixture (*A*) of substances which is partly acetylated (Ac_2O–C_5H_5N at room temp.) and then subjected to chromatography, thereby giving the well-cryst. allo*pregnane*-3(β) : 17(α) : 20(α) : 21-*tetraol* 3 : 17 : 21-*triacetate* (**I**), m.p. 120—121°, $[\alpha]_D^{15}$ −31·5°±4°, $[\alpha]_{5461}^{15}$ −38·5° ±4° in $COMe_2$, and allo*pregnane*-3(β) : 17(α) : 21-*triol*-20-*one triacetate* (**II**), m.p. 178—180° (softens at 173°), $[\alpha]_D^{15}$ −12·8°±5°, $[\alpha]_{5461}^{15}$ −18·9°±5° in $COMe_2$. In one experiment a small amount of allo*pregnane*-3(β) : 17(α) : 21-*triol*-20-*one* 3 : 21-*diacetate* (**III**), m.p. 158—161°, $[\alpha]_D^{19}$ −55·7°±2°, $[\alpha]_{5461}^{19}$ −66·7°±2° in $COMe_2$, was isolated; the production of this is due to acyl migration. Attempted separation of (*A*) by crystallisation from Et_2O gave an allo*pregnanetetraol diacetate*, m.p. 160—162°, $[\alpha]_D^{18}$ −18·6°±2°, $[\alpha]_{5461}^{18}$ −26°±2° in $COMe_2$, oxidised (CrO_3) to androstan-3(β)-ol-17-one acetate. An allo*pregnanetetraol tetra-acetate*, m.p. 252—256°, $[\alpha]_D^{18}$ −28·0°±5°, $[\alpha]_{5461}^{18}$ −33·7°±6° in $COMe_2$, which is not derived from (**I**), is described. (**I**) is oxidised by CrO_3 to (**II**) and is distinguished from (**IV**) (below) only by this method. (**I**) is converted by energetic hydrolysis followed by re-acetylation into *allo*pregnane-3(β) : 17(α) : 20(α) : 21-tetraol 3 : 20 : 21-triacetate (**IV**), m.p. 119—121°. (**II**) is hydrolysed ($KHCO_3$ in MeOH at room temp.) to a mixture which is re-acetylated to (**II**) and degraded by HIO_4 in aq. MeOH at room temp. followed by hydrolysis to 3(β) : 17(α)-dihydroxyætio*allo*cholanic acid (**V**). Successive hydrogenation (Raney Ni under pressure), energetic hydrolysis, and re-acetylation of (**II**) affords (**IV**). Ac at $C_{(17)}$ in (**II**) cannot be simply removed without disturbing the mol. structure of the residue. Δ^{20}-*allo*Pregnene-3(β) : 17(α)-diol 3-monoacetate is similarly converted by the successive actions of OsO_4 and $HClO_3$ in Et_2O into a mixture from which, after acetylation, (**III**), m.p. 160—162°, is isolated in 6% yield. It is hydrolysed ($KHCO_3$ in aq. MeOH) at 20° to a mixture of the free OH-ketone (**VI**) and its 3-*monoacetate*, m.p. 195—197°, $[\alpha]_D^{19}$ −42·9°±3° in $COMe_2$; crude (**VI**) is oxidised by HIO_3 to (**V**). $\Delta^{4:20}$-Pregnadien-17(α)-ol-3-one (**VII**) and boiling C_5H_5N–Ac_2O give the *acetate* (**VIII**), m.p. 120—122°, $[\alpha]_D^{15}$ +82·7°±3° in $COMe_2$, also obtained by the oxidation [$Al(OBu^t)_3$, $COMe_2$, C_6H_6] of $\Delta^{5:20}$-*pregnadiene*-3(β) : 17(α)-*diol* 17-*monoacetate*, m.p. 172—174° (from the diacetate and aq. MeOH–$KHCO_3$). (**VIII**) is treated successively with OsO_4 and $HClO_3$, partly acetylated, and oxidised to a product from which Δ^4-pregnene-17(α) : 21-diol-3 : 20-dione diacetate could not be isolated. Similar treatment of (**VII**) leads to two substances, m.p. 149—151°, $[\alpha]_D^{19}$ +13·4°±2° in $COMe_2$, and m.p. 265—268°, $[\alpha]_D^{14}$ +58·4°±4° in dioxan, the structures of which are not elucidated. H. W.

Glucosides of deoxycorticosterone.—See A., 1942, II, 219.

Steroids and sex hormones. LXXVI. Preparation of a digitaloid aglucone by oxidation of methyl 3(β)-acetoxy-$\Delta^{20:22}$-nor*allo*cholenate by selenium dioxide. L. Ruzicka, P. A. Plattner, and J. Pataki (*Helv. Chim. Acta*, 1942, **25**, 425—435).—Pregnenolone acetate, Zn, and $CH_2Br{\cdot}CO_2Et$ in C_6H_6 give (after hydrolysis) 3(β) : 20-*dihydroxy*-Δ^5-*norcholenic acid*, m.p. 204—206°, $[\alpha]_D^{17}$ −47·1°±2° in EtOH [*Me* ester, m.p. 131—133°, $[\alpha]_D^{17}$ −55·8°±1° in $CHCl_3$, and its 3-*acetate* (**I**), m.p. 146—147°, $[\alpha]_D^{17}$ −58·8°±2° in $CHCl_3$]. (**I**) is converted slowly by boiling Ac_2O or more rapidly by $KHSO_4$ at 180—190°/high vac. into *Me* 3(β)-*acetoxy*-$\Delta^{5:6\text{-}20:22}$-*norcholadienate*, m.p. 147—149°, $[\alpha]_D^{17}$ −54·4°±1° in $CHCl_3$, hydrolysed by boiling KOH–MeOH to

3(β)-*hydroxy*-Δ$^{5:6\text{-}20:22}$-*norcholadienic acid*, m.p. 262—265°, $[\alpha]_D^{14}$ −49·8°±2° in dioxan (*Me* ester, m.p. 139—142°, $[\alpha]_D^{14\cdot8}$ −50·2°±1° in $CHCl_3$). Hydrogenation (PtO_2 in AcOH) of (I) gives *Me* 20-*hydroxy*-3(β)-*acetoxynor*allo*cholanate* (II), m.p. 180—181°, $[\alpha]_D^{17}$ +3·5°±1° in $CHCl_3$, hydrolysed to 3(β) : 20-*dihydroxynor*allo*cholanic acid*, m.p. 201—202°, $[\alpha]_D^{15}$ +9·2°±1° in EtOH (*Me* ester, m.p. 163—165·5°, $[\alpha]_D^{15}$ +6°±1° in $CHCl_3$). Boiling Ac_2O slowly transforms (II) into *Me* 3(β)-*acetoxy*-Δ$^{20:22}$-*nor*allo*cholenate* (III), m.p. 161—163°, $[\alpha]_D^{18}$ +6·3°±0·5° in $CHCl_3$, whence 3(β)-*hydroxy*-Δ$^{20:22}$-*nor*allo*cholenic acid*, m.p. 237—239°, $[\alpha]_D^{18}$ +0·5°±1° in EtOH (*Me* ester, m.p. 148—150° after softening at 131°, $[\alpha]_D^{17}$ +10·9°±1° in $CHCl_3$). (III) is oxidised by SeO_2 to 21-hydroxy-3(β)-acetoxy-Δ$^{20:22}$-nor*allo*cholenolactone, m.p. 192—196°, $[\alpha]_D^{15}$ −0·7°±2° in $CHCl_3$. M.p. are corr. (vac.). H. W.

Steroids and sex hormones. LXXVII. Homologue of the digitaloid aglucone ; β′-[3(β)-hydroxy-Δ^5-23-norcholenyl]-Δ$^{\alpha}$′$^{\beta}$′-butenolide. L. Ruzicka, P. A. Plattner, and H. Heusser (*Helv. Chim. Acta*, 1942, **25**, 435—438).—3(β)-Hydroxy-Δ^5-cholenic acid, m.p. 236—237°, $[\alpha]_D$ −39·4° in C_5H_5N, is converted into its acetate, and thence into the acid chloride and diazo-ketone, which with AcOH at 95° gives

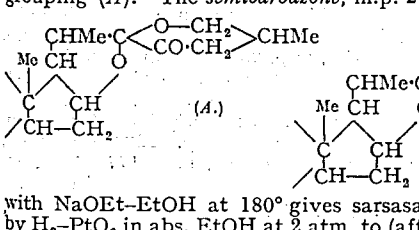


(I.)

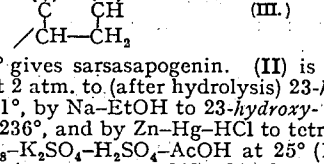
Δ^5-24-*keto*-3(β) : 25-*diacetoxy*-25-*homocholene* (I), m.p. 125·5—126°, $[\alpha]_D$ −45·06° in $CHCl_3$. Zn and $CH_2Br{\cdot}CO_2Et$ convert (I) into essentially β′-hydroxy-β′-[3(β)-hydroxy-Δ^5-23-norcholenyl]-γ′-butanolide, transformed by Ac_2O at 153° (bath) into β′-[3(β)-*acetoxy*-Δ^5-23-*norcholenyl*]-Δ$^{\alpha}$′$^{\beta}$′-*butenolide*, m.p. 204—205°, $[\alpha]_D$ −40·55° in $CHCl_3$, hydrolysed to the 3(β)-*OH*-derivative, m.p. 229—230°, $[\alpha]_D$ −42·52° in $CHCl_3$. M.p. are corr. (vac.). H. W.

Sterols. CXXXVI. Sapogenins. LVII. Structure of the side-chain of chlorogenin. R. E. Marker, D. L. Turner, and E. L. Wittbecker (*J. Amer. Chem. Soc.*, 1942, **64**, 809—812).—The structure of chlorogenin is confirmed and differs from that of β-chlorogenin (I) only in the configuration of the OH at $C_{(6)}$. Zn–Hg in conc., aq. HCl + EtOH reduces chlorogenone to deoxychlorogenin (= deoxytigogenin) (II) and a carbinol, converted by PBr_3 and then H_2–PtO_2 in abs. EtOH into cholestane. With, successively, Ac_2O at 200°, boiling KOH–MeOH, CrO_3–AcOH at 30°, and KOH–MeOH–H_2O, (II) gives Δ^{16}-*allo*pregnen-20-one and thence *allo*pregnan-20-one. Ac_2O at 200° and then KOH converts (I) into *ψ-β-chlorogenin* (III), m.p. 180—182°, reconverted into (I) by boiling conc. aq. HCl–MeOH and oxidised by CrO_3–AcOH at 25° to $CO_2H{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}CO_2H$ and Δ^{16}-*allo*pregnene-3 : 6 : 20-trione (IV) and thence (H_2–PtO_2–AcOH; 45 lb.) *allo*pregnane-3(β) : 6(β) : 20(β)-triol (V). Acetylation of (III) prior to oxidation as above gives, after hydrolysis, Δ^{16}-allo*pregnene*-3(β) : 6(β)-*diol*-20-*one*, m.p. 214—216° (*diacetate*, m.p. 233—235°), oxidised by CrO_3 to (IV) and hydrogenated to (V). R. S. C.

Sterols. CXXXVII. Sapogenins. LVIII. Oxidation products of sarsasapogenin : ketosarsasapogenin. R. E. Marker and A. C. Shabica (*J. Amer. Chem. Soc.*, 1942, **64**, 813—816).—23-Keto-sarsasapogenin (I), m.p. 225—226° [best purified by way of the *acetate* (II), m.p. 172—173°; cf. A., 1939, II, 31, 510], contains the grouping (*A*). The *semicarbazone*, m.p. 291—293° (decomp.), of (I)



(*A*.)



(III.)

with NaOEt–EtOH at 180° gives sarsasapogenin. (II) is reduced by H_2–PtO_2 in abs. EtOH at 2 atm. to (after hydrolysis) 23-*hydroxy-dihydro*- (III), m.p. 219—221°, by Na–EtOH to 23-*hydroxy*- (*A* with CH·OH for CO), m.p. 234—236°, and by Zn–Hg–HCl to tetrahydro-sarsasapogenin. With $K_2S_2O_8$–K_2SO_4–H_2SO_4–AcOH at 25° (16 days) and later KOH–EtOH, (I) gives pregnane-3(β) : 16 : 20-triol, m.p. 221—222°, and the OH-lactone (IV), $C_{22}H_{34}O_3$. With CrO_3–AcOH at 60°, and later aq. NaOH, (II) gives (IV) and some of the CO-acid, $C_{22}H_{34}O_4$, but no sarsasapogenoic acid. R. S. C.

Sterols. CXXXIX. Sapogenins. LIX. Bio-reduction of 4-dehydrotigogenone. R. E. Marker, E. L. Wittbecker, R. B. Wagner, and D. L. Turner (*J. Amer. Chem. Soc.*, 1942, **64**, 818—822; cf. A., 1936, 1386).—Smilagenone is reduced (H_2, PtO_2, EtOH or Na, EtOH) to epi*smilagenin* (epi-iso*sarsasapogenin*) (I), m.p. 217—220° (*acetate*, m.p. 158—159°), and is regenerated therefrom by CrO_3–AcOH at 25°. Hydrogenation (PtO_2) of (I) in AcOH at 70—75°/3 atm. gives dihydro*epi*sarsasapogenin, dimorphic, m.p. 134—136° and 180—182°. R. S. C.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Inactivation in the camphene series. J. J. Ritter and G. Vlases, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 583—585).—ω-Hydroxymethyl-camphene, b.p. 120—125°/10 mm., $[\alpha]_D^{20}$ +24·0° (acetate, b.p. 130—138°/20 mm., $[\alpha]_D^{20}$ +18·9°), with PCl_3 in light petroleum gives the CH_2Cl derivative (71%), b.p. 109—111°/15 mm., $[\alpha]_D^{20}$ +18·5°, which with MgRHal in Et_2O gives *ω-β-phenylethyl-* (I) (81%), b.p. 138—140°/5 mm., $[\alpha]_D^{25}$ +0·66° (*hydrochloride*, m.p. 58—60°; *hydrobromide*, an oil, dissociates when distilled; Br adduct), ω-n-*propyl-* (34%), b.p. 104—106°/45 mm., $[\alpha]_D^{20}$ +16·4° (*hydrochloride*; Br adduct), ω-n-*hexyl-* (II) (51%), b.p. 124°/15 mm., $[\alpha]_D^{20}$ +17·8° [*hydrochloride* (III); Br adduct], and ω-cyclo*hexylmethyl-camphene* (45%), b.p. 133°/4 mm., $[\alpha]_D^{20}$ +16·5° (*hydrochloride*; Br adduct). In boiling NH_2Ph, (III) gives probably a mainly racemised (II), $[\alpha]_D^{20}$ +0·20°. With NH_2Ph,HBr in boiling NH_2Ph, (I) is probably only racemised (product, $[\alpha]_D^{25}$ +0·10°). In $CCl_3{\cdot}CO_2H$ at 40° (several days), (II) gives an ester, hydrolysed to *amyl*iso*borneol*, m.p. 63—64°, b.p. 105—120°/1 mm. Failure to yield an active position isomeride rebuts the theory of Lipp *et al.* (A., 1932, 398). The racemisation probably occurs by 1 : 6 pinacol change. R. S. C.

Sesquiterpenes. LI. Constitution of cedrenene. L. Ruzicka, P. A. Plattner, and G. W. Kusserow (*Helv. Chim. Acta*, 1942, **25**, 85—95).—The cedrene fraction of cedar-wood oil is converted by moist O_2 into cedrenol, m.p. 103·5—104°, dehydrated by boiling Ac_2O to cedrenene (I), b.p. 122°/11 mm. Under mild conditions (I) does not react with $(CH{\cdot}CO)_2O$, whilst at higher temp. insol. heteropolymerides result. With $(CO_2Me{\cdot}C)_2$ at 180°, (I) gives ~25% of polymerides and ~35% of the normal *adduct*, $C_{12}H_{28}O_4$, m.p. 132—132·5°, $[\alpha]_D$ +83° in MeOH. This distils unchanged under room pressure. It is hydrolysed to an *acid*, $C_{10}H_{24}O_4$, m.p. 230°, and hydrogenated (PtO_2 in AcOH) to the *compound*, $C_{21}H_{32}O_4$, m.p. 123·5—125°, $[\alpha]_D$ −62° in MeOH, which is saturated towards $C(NO_2)_4$. (I) in freshly distilled $CHCl_3$ under CO_2 is quantitatively converted by Br into the dibromide, m.p. 90—91°, converted by boiling KOH–MeOH into the *substance*, $C_{16}H_{25}OBr$, m.p. 149—150°; a Br-free product could not be obtained by prolonged action of KOH–MeOH, KOH–60% dioxan, or of NaOAc in boiling AcOH, C_5H_5N, or 2 : 6-dimethylpyridine. (I) is oxidised by $KMnO_4$ in aq. $COMe_2$ to norcedrenedicarboxylic acid (II), m.p. 212·5—213°, $[\alpha]_D$ −39° in $CHCl_3$; this with boiling Ac_2O gives the *anhydride*, m.p. 128—128·5°, $[\alpha]_D$ +50° in $CHCl_3$, hydrolysed by aq. dioxan to (II). Cedrenedicarboxylic acid is similarly transformed into its *anhydride*, m.p. 79—82°. M.p. are corr. H. W.

Triterpenes. LXIII. Oxidation of betulin diacetate with monoperphthalic acid and selenium dioxide. L. Ruzicka, M. Brenner, and E. Rey (*Helv. Chim. Acta*, 1942, **25**, 161—170).—The experience gained in the oxidation of lupeol has been applied to that of betulin. Betulin diacetate (I) is converted by *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ in $CHCl_3$ into its *oxide* (II), m.p. 198—205° after softening at 190°, which gives no yellow colour with $C(NO_2)_4$ and (absorption spectrum) does not contain CHO. (II) is isomerised by boiling EtOH or aq. dioxan into diacetoxylupanal (III), m.p. 248—253° (softens at 230°), and by boiling KOH–MeOH into *dihydroxylupanal*, m.p. 263—272° (*oxime*, m.p. ~230°). Oxidation of (II) with CrO_3 gives the mixture of stereoisomeric diacetoxylupanic acids (characterised as esters) identical with the products obtained similarly from (I); the neutral by-products include diacetoxynorlupanone and (III). (I) is oxidised by SeO_2 in boiling AcOH or Ac_2O or in C_6H_6 at 160° to *diacetoxy-lupenal* (IV), m.p. 249—251°, $[\alpha]_D$ +8·4° in $CHCl_3$, which gives a pale yellow colour with $C(NO_2)_4$. Hydrolysis (N-KOH–EtOH) of (IV) affords *dihydroxylupenal*, m.p. 254°, $[\alpha]_D$ −2·5° in $CHCl_3$ [*oxime* (V), m.p. 201°]. Boiling Ac_2O and (V) afford *diacetoxylupenonitrile*, m.p. 234°, $[\alpha]_D$ +14·7° in $CHCl_3$, which does not give a yellow colour with $C(NO_2)_4$ and is hydrogenated (Pd–$CaCO_3$ in EtOH–dioxan) to *diacetoxylupanonitrile*, m.p. 275°, $[\alpha]_D$ +12° in $CHCl_3$. (IV) is hydrogenated (PtO_2 in AcOH) to trihydroxylupan diacetate, converted by Ac_2O–C_5H_5N at room temp. into *triacetoxylupan*, m.p. 140—141°, $[\alpha]_D$ −1·2° in $CHCl_3$, and oxidised by CrO_3 to (+)-diacetoxylupanic acid, identified as the Me ester, m.p. 234—235°, $[\alpha]_D$ +17·0° in $CHCl_3$. M.p. are corr. (vac.). H. W.

Triterpenes. LXIV. Degradation of betulin diacetate by ozone. L. Ruzicka and E. Rey (*Helv. Chim. Acta*, 1942, **25**, 171—179).—Treatment of betulin diacetate in $CHCl_3$–EtOAc with 3—4% O_3 and decomp. of the ozonide with boiling N-KOH–MeOH gives almost equal amounts of acid and neutral products. The former with CH_2N_2 give *Me dihydroxybisnorlupanate* (I), m.p. 268°, $[\alpha]_D$ −5·7° in $CHCl_3$ (*diacetate*, m.p. 226—227°, $[\alpha]_D$ −13·7° in $CHCl_3$), hydrolysed by alkali to the *acid*, m.p. 312°, $[\alpha]_D$ −2·4° in dioxan. The latter yields diacetoxynorlupanone (II), m.p. 190—191°, $[\alpha]_D$ −11·3° in $CHCl_3$, converted by Br–KOH followed by CH_2N_2 into (I). (I) is transformed by an excess of MgPhBr in Et_2O–C_6H_6 into *triacetoxy-diphenylbisnorlupan*, m.p. 235—237°, $[\alpha]_D$ −24·8° in $CHCl_3$, which gives no colour with $C(NO_2)_4$. With MgMeI in Et_2O–PhOMe (II) affords *diacetoxyisolupene* (iso*betulin diacetate*), m.p. 210°, $[\alpha]_D$ +15° in $CHCl_3$. Chromatographic purification of dicarboxylic acid *A*, obtained by the oxidation of betulin monoacetate with CrO_3, leads to a product, $C_{32}H_{50}O_6$, m.p. 310°, $[\alpha]_D$ −44·5° in $CHCl_3$ (Me_2 ester, m.p. 182°, $[\alpha]_D$ −44·2° in $CHCl_3$); acids *A* and *E* are therefore stereoisomeric hydroxylupandicarboxylic acids. H. W.

Triterpenes. XLV. β-Elemonic acid. L. Ruzicka and H. Häusermann (*Helv. Chim. Acta*, 1942, **25**, 439—457).—The mixture

of acids from Manila elemi resin is purified by crystallisation from EtOH and separated by Girard's reagent *T* into α-elemolic acid (**I**) and β-elemonic acid, $C_{30}H_{46}O_3$ (**II**), m.p. 224—225°, $[\alpha]_D$ +47·6° in $CHCl_3$ [Me ester (**III**), m.p. 104—105°, $[\alpha]_D$ +35° in $CHCl_3$]. Hydrogenation (PtO_2 in AcOH–EtOH) of (**II**) gives *dihydro-β-elemolic acid* (**IV**), m.p. 251—252°, $[\alpha]_D$ +15·1° in $CHCl_3$ (*acetate*, m.p. 266—267°, $[\alpha]_D$ +15·6° in $CHCl_3$), which gives a yellow colour with $C(NO_2)_4$. Esterification and acetylation of the compounds contained in the mother-liquors from (**IV**) leads to the isolation of Me acetyldihydro-α-elemolate (**V**), m.p. 139—140°, $[\alpha]_D$ −33·1° in $CHCl_3$. Under similar conditions (**III**) is hydrogenated and subsequently acetylated to *Me acetyldehydro-β-elemolate* (**VI**), m.p. 137—137·5°, $[\alpha]_D$ +14·2° in $CHCl_3$, which gives a marked yellow colour with $C(NO_2)_4$. In presence of Pd–C in AcOH at room temp. (**II**) is hydrogenated to *dihydro-β-elemonic acid* (**VII**), m.p. 245—246°, $[\alpha]_D$ +37·5° in $CHCl_3$ [*oxime*, m.p. 240° (decomp.)], which gives a yellow colour with $C(NO_2)_4$. With Raney Ni as catalyst and H_2 at 125°/70 atm. (**II**) gives (**VII**); acetylation and esterification of the acid residue leads to the isolation of (**VI**) and (**V**). Na and $Bu^{\beta}OH$ reduce (**II**) to *β-elemolic acid*, m.p. 234—235°, $[\alpha]_D$ +9·5° in $CHCl_3$ (*acetate*, m.p. 248—249°, $[\alpha]_D$ +25·6° in $CHCl_3$), hydrogenated (PtO_2 in AcOH) to (**IV**) which is oxidised (CrO_3 in AcOH) to (**VII**). *Acetyldihydro-β-elemolyl chloride*, m.p. 178—179°, from the acid and $SOCl_2$ in *n*-hexane, is reduced (Rosenmund) to *acetyldihydro-β-elemolaldehyde*, m.p. 167—168°, $[\alpha]_D$ +11·5° in $CHCl_3$ (*oxime*, m.p. 93—95°); the *semicarbazone* is reduced (Wolff–Kishner) to *dihydro-β-tritelemol*, m.p. 146—147°, $[\alpha]_D$ ±0° in $CHCl_3$ (*acetate*, m.p. 146°, $[\alpha]_D$ −0·41° in $CHCl_3$; *benzoate*, m.p. 155·5—156°), which gives a marked yellow colour with $C(NO_2)_4$; it is oxidised by CrO_3 in AcOH to *dihydro-β-tritelemone*, $C_{30}H_{50}O$, m.p. 66—67°, $[\alpha]_D$ +32·3° in $CHCl_3$. Reduction (Bouveault–Blanc) of Me β-elemonate affords *β-tritelemidiol*, $C_{30}H_{50}O_2$, m.p. 179—180°, $[\alpha]_D$ −7° in $CHCl_3$. (**II**) or (**III**) is reduced (Wolff–Kishner) to *deoxo-β-elemonic acid*, $C_{30}H_{48}O_2$, m.p. 236—237°, $[\alpha]_D$ +10·45° in $CHCl_3$. A great similarity in structure of (**I**) and (**II**) is thus established but the difference between them cannot consist solely of a difference in the position of the more readily hydrogenated double linking. M.p. are corr. (vac.).

H. W.

Triterpenes. LXVI. Introduction of double linkings and carbonyl groups into the rings C—E of β-amyrin. L. Ruzicka, O. Jeger, and J. Norymberski (*Helv. Chim. Acta*, 1942, **25**, 457—463).—β-Amyrin acetate is oxidised by SeO_2 in dioxan at 200° to β-amyradienedionol acetate, m.p. 239° (converted by N_2H_4,H_2O in EtOH at 200° into the pyridazine derivative, $C_{30}H_{44}ON_2$, m.p. 292—293°), also obtained by the similar oxidation of β-amyradienol 11-acetate (**I**) and δ-amyrin acetate. The latter substance is oxidised by 30% H_2O_2 in boiling AcOH to the corresponding *oxide* (**II**), m.p. 266—267°, which is saturated towards $C(NO_2)_4$, does not react with Ac_2O–C_5H_5N at 80°, and is indifferent towards H_2O–dioxan at 200—210°. (**II**) is transformed by boiling AcOH containing conc. HCl into (**I**). $Pb(OAc)_4$ in AcOH–C_6H_6 oxidises (**I**) to β-amyradienonol acetate, m.p. 258—259°, $[\alpha]_D$ +336° in $CHCl_3$.

H. W.

VI.—HETEROCYCLIC.

Action of benzoyl chloride on ethyl β-diethylaminocrotonate.—See A., 1942, II, 261.

Reaction between quinones and metallic enolates. XVI. Dibromo-*o*-xyloquinone and sodiomalonic ester. L. I. Smith and F. L. Austin (*J. Amer. Chem. Soc*, 1942, **64**, 524—527; cf. A., 1941, II, 201).—The mode of interact on of $CHNa(CO_2Et)_2$ (**I**) with dibromodimethylquinones depends on the relative positions of the Br rather than Br and Me (cf. A., 1937, II, 255; 1941, II, 144). *o*-Xyloquinone is best (61%) obtained from *o*-3-xylenol by successive treatment with *p*-$SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$, $Na_2S_2O_4$, and $Fe_2(SO_4)_3$–aq. H_2SO_4. With Br–$CHCl_3$ at room temp. it gives 4 : 5-*dibromo*-2 : 3-*dimethylbenzoquinone*, m.p. 152·5—153°, reduced by $SnCl_2$–aq. HCl–EtOH to the *quinol*, m.p. 163—164°, and by Zn dust and H_2SO_4 in Ac_2O–AcOH to the *quinol diacetate*, m.p. 203—206°, and with (**I**) in dioxan (not under other conditions) gives successively 5-*bromo*-6-*dicarbethoxymethyl*-, b.p. 115—120°/1 mm., isolated by way of the *quinol* (**II**), m.p. 126—127° [*diacetate* (**III**), m.p. 92—93°], and 5 : 6-*bisdicarbethoxymethyl*-2 : 3-*dimethylbenzoquinone*, m.p. 83—84°. With 75% H_2SO_4 at room temp., (**II**) in $CHCl_3$ gives 3-*bromo*-4-*hydroxy*-2-*carbethoxy*-5 : 6-*dimethylisocoumaranone* (**IV**), m.p. 109—110° [*acetate* (**V**), m.p. 117—118°], converted in boiling AcOH into 3-*bromo*-4-*hydroxy*-5 : 6-*dimethylisocoumaranone* (**VI**), m.p. 155—156° [*acetate*, m.p. 195—197°, also obtained from (**V**) by boiling AcOH], which is obtained also from (**II**) by boiling AcOH containing a trace of Zn and from (**III**) by boiling HCl–AcOH. Me_2SO_4–KOH–MeOH converts (**II**) into 3-*bromo*-2-*carboxy*-1 : 4-*dimethoxy*-5 : 6-*dimethylcoumarone*, m.p. 141—143°, converted by distillation in steam into 3-*bromo*-4-*methoxy*-5 : 6-*dimethylisocoumaranone* (**VII**), m.p. 113—113·5°, which is also (m.p. 108—110°) obtained from (**IV**) by Me_2SO_4–KOH–MeOH, followed by acidification and distillation of the resultant oil in steam. *o-Xyloquinol Me*$_2$ *ether* (prep. from the quinol by Me_2SO_4–KOH–MeOH), m.p. 78°, is unaffected by morpholine–CH_2O–EtOH at 100°, but with 40% CH_2O–HCl (exothermally and then at 100°) gives 2 : 5-*dimethoxy*-3 : 4-*dimethylbenzyl chloride* (52%), m.p. 67—68°, b.p. 162—163°/25 mm. [and some ? $(CH_2Cl)_2$ compound], which with KCN in EtOH containing a little H_2O at 100° gives the *cyanide* (55%), m.p. 95—96°, and thence by boiling 1 : 1 : 1 H_2SO_4–AcOH–H_2O 2 : 5-*dimethoxy*-3 : 4-*dimethylphenylacetic acid* (44%), m.p. 120—121°. With Br–$CHCl_3$ at room temp. this gives 6-*bromo*-2 : 5-*dimethoxy*-3 : 4-*dimethylphenylacetic acid*, m.p. 154—155°, also obtained from (**VI**) by Me_2SO_4–KOH–MeOH and from (**VII**) by KOH–MeOH. This proves the structure of the products named above.

R. S. C.

New reactions of 1-benzylidenecoumaran-2-ones. II. T. B. Panse, R. C. Shah, and T. S. Wheeler (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 83—85).—Bromination of 2-acetoxy-4-methoxyphenyl *p*-methoxystyryl ketone in CCl_4 leads to 2-*acetoxy*-4-*methoxyphenyl* αβ-*dibromo*-β-p-*anisylethyl ketone*, m.p. 143°, converted by boiling EtOH followed by boiling 10% KOH into 5-*methoxy*-1-p-*anisylidenecoumaran*-2-*one* (**I**), m.p. 134°. This is converted by Br in cold $CHCl_3$ into 1-*bromo*-5-*methoxy*-1-ω-*bromo*-p-*methoxybenzylcoumaran*-2-*one* (**II**), m.p. 161°. When boiled with the requisite alcohol (**II**) affords 1-*bromo*-5-*methoxy*-1-ω : p-*dimethoxybenzyl*-, m.p. 131°, and 1-*bromo*-5-*methyl*-1-p-*methoxy*-ω-*ethoxybenzyl*-, m.p. 139°, -*coumaran*-2-*one*. (**II**) and *cyclo*hexanone in boiling NaOH–EtOH yield 5-*methoxy*-1-p-*methoxy*-ω-2′-*keto*cyclo*hexylbenzylcoumaran*-2-*one*, m.p. 182° (decomp.). With CH_2PhBz and NaOEt in boiling EtOH (**I**) gives 5-*methoxy*-1-*benzoyl*-β-*phenyl*-α-p-*anisyl*-α-*ethylcoumaran*-2-*one*, m.p. 273°. $CH_2Ac{\cdot}CO_2Et$ and (**I**) afford *Et* 2-p-*anisyl*-3 : 4-[1′′ : 2′-(5′-*methoxycoumarano*)]-Δ^4-cyclo*hexen*-6-*one*-1-*carboxylate*, m.p. 146°, hydrolysed and decarboxylated by 10% HCl at 160° to 5-p-*anisyl*-3 : 4-[2′ : 1′-(5′-*methoxycoumarano*)]-Δ^2-cyclo*hexen*-1-*one*, m.p. 154° [*semicarbazone*, m.p. 246° (decomp.); *oxime*, m.p. 142°; 2 : 4-*dinitrophenylhydrazone*, m.p. 912°; *Cu* salt, m.p. 215°].

H. W.

Chemistry and biochemistry of plant substances. VII. Formation of hydroxy-chalkones and -flavanones. L. Reichel, W. Burkart, and K. Müller (*Annalen*, 1942, **550**, 146—161; cf. A., 1939, III, 219).—2 : 4 : 1-$(OH)_2C_6H_3{\cdot}COMe$ or 2 : 4 : 6 : 1-$(OH)_3C_6H_2{\cdot}COMe$ and 3 : 4 : 1-$(OH)_2C_6H_3{\cdot}CHO$ in EtOH–aq. NaOH at 60° or in a borate–NaOH buffer (p_H 10·9) at 37° for 30 days (in N_2) give 3 : 4 : 2′ : 4′-tetrahydroxychalkone (butein), m.p. 198°, or 5 : 7 : 3′ : 4′-tetrahydroxyflavanone (eriodictyol), m.p. 267°, respectively. *o*-$OH{\cdot}C_6H_4{\cdot}COMe$ (**I**), 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}CHO$ (**II**), and aq. NaOH at 37° (p_H 10·65) for 7 days afford 3′ : 4′-*dimethoxyflavanone*, m.p. 125°. (**I**) and piperonal in aq. NaOH (p_H 10·74 at 37° for 15 days) give 2′-*hydroxy*-3 : 4-*methylenedioxychalkone*, m.p. 138°, and 3′ : 4′-*methylenedioxyflavanone*, m.p. 129°. 2 : 4 : 6 : 1-$(OMe)_2C_6H_2(OH){\cdot}COMe$ and PhCHO or (**II**) in aq. NaOH (p_H 11·8) at 37° yield 5 : 7-dimethoxyflavanone, m.p. 145°, or 2-hydroxy-3 : 4 : 4′ : 6′-tetramethoxychalkone, m.p. 151°, respectively.

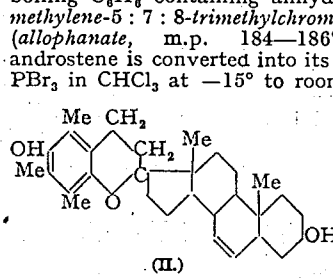
A. T. P.

Condensation of α-substituted acetoacetates with phenols. V. Coumarins from alkylresorcinols, and ethylpyrogallol and ethyl α-β′β′β′-trichloro-α′-hydroxyethylacetoacetate. N. M. Shah and D. R. Kulkarni (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 86—88).—The alkyl group has no retarding influence on the course of the reaction. Gradual addition of $POCl_3$ to a cooled mixture of 4 : 1 : 3-$C_6H_3Et(OH)_2$ and $CCl_3{\cdot}CH(OH){\cdot}CHAc{\cdot}CO_2Et$ gives 7-*hydroxy*-4-*methyl*-6-*ethyl*-3-βββ-*trichloro*-α-*hydroxyethylcoumarin* (**I**), m.p. 211—212° (decomp.), also obtained in poor yield when 80% H_2SO_4 is used as condensing agent. (**I**) gives a blue fluorescence in alkali and a violet fluorescence in conc. H_2SO_4. The *Ac*, m.p. 167°, *Bz*, m.p. 185—186°, *Me*$_2$, m.p. 167° and *Me*$_1$, m.p. 231° (decomp.), derivatives are described. Similarly, 4 : 1 : 3-$C_6H_3Pr(OH)_2$ affords 7-*hydroxy*-4-*methyl*-6-*propyl*-3-βββ-*trichloro*-α-*hydroxyethylcoumarin*, m.p. 189° (*acetate*, m.p. 132—134°), in poor yield. 7 : 8-*Dihydroxy*-4-*methyl*-6-*ethyl*-3-βββ-*trichloro*-α-*hydroxyethylcoumarin*, m.p. 223° (decomp.), from 4 : 1 : 2 : 3-$C_6H_2Et(OH)_3$, and its *acetate*, m.p. 177—178°, are described.

H. W.

Coumarins etc.—See B., 1942, II, 220.

Syntheses of chroman derivatives with tocopherol-like structure. P. Karrer and F. Kehrer (*Helv. Chim. Acta*, 1942, **25**, 29—34).—*cyclo*Hexanone and C_2H_2 in presence of $NaNH_2$ yield 1-*acetylenyl*cyclo*hexan*-1-*ol*, b.p. 80—83°/20 mm., hydrogenated (Pt in EtOH) to 1-*vinyl*cyclo*hexan*-1-*ol*, b.p. 75—77°/10 mm. This is converted by PBr_3 in light petroleum at −15° to 18° into cyclo*hexylidene*-*ethyl bromide*, b.p. 90—93°/20 mm., which with trimethylquinol (**I**) in boiling C_6H_6 containing anhyd. $ZnCl_2$ gives 6-*hydroxy*-2 : 2-*pentamethylene*-5 : 7 : 8-*trimethylchroman*, a viscous, strongly reducing oil (*allophanate*, m.p. 184—186°). Δ^5-3*t* : 17*t*-Dihydroxy-17-vinylandrostene is converted into its *acetate*, m.p. 160—161°, which with PBr_3 in $CHCl_3$ at −15° to room temp. gives 17-β-*bromoethylidene*-Δ^5-3*t*-*acetoxyandrostene*, which does not solidify at −8°; it condenses with (**I**) to spiro-2-[6-*hydroxy*-5 : 7 : 8-*trimethylchroman*]-17′-[3′-*hydroxy*-Δ^5′-*androstene*] (**II**), m.p. 226—228°, which reduces alcoholic $AgNO_3$ and can be determined colorimetrically with $FeCl_3$ and 2-dipyridyl. Me pentadecyl ketone,



(II.)

C_2H_2, and $C_5H_{11}{\cdot}OK$ give γ-*hydroxy*-γ-*methyl*-Δ$^{\alpha}$-*octadecinine*, b.p.

129—134°/0·23 mm., m.p. 25°, reduced (H_2–Pt–EtOH) to *γ-hydroxy-γ-methyl-*Δ^{α}*-octadecene*, b.p. 155—159°/0·7 mm., m.p. ~27°. This with PBr_3 in light petroleum at −15° to room temp. yields α-bromo-γ-methyl-Δ^{β}-octadecene, condensed with (I) to 6-*hydroxy*-2 : 5 : 7 : 8-*tetramethyl*-2-*pentadecylchroman*, m.p. 68°, which has great reducing power. H. W.

1 : 3-Dioxans.—See B., 1942, II, 255.

5 : 7-Dimethyltocol formate.—See B., 1942, III, 157.

Oreoselone. F. von Bruchhausen and H. Hoffmann (*Ber.*, 1942, **75**, [*B*], 146—147; cf. A., 1931, 1298).—The m.p. of dihydro-oreoselonic acid (I) depends greatly on the rate of heating. (I) can be sublimed at 165°/0·01 mm., or 165°/0·15 mm., without appreciable conversion into the lactone. H. W.

2-Thienylalkylamines. F. F. Blicke and J. H. Burckhalter (*J. Amer. Chem. Soc.*, 1942, **64**, 477—480).—The pressor activity of the 2-thienylalkylamines named below is semiqualitatively equal to that of the corresponding phenylalkylamines. 2-Thienylcarbinol (obtained from MgRI and CH_2O) with PBr_3 gives the bromide, which with $(CH_2)_6N_4$ in boiling $CHCl_3$ yields exothermally an adduct (72%), m.p. 160—161° (decomp.), converted by HCl–abs. EtOH into 2-thienylmethylamine, $NH_2{\cdot}CH_2{\cdot}C_4H_3S$, b.p. 73—75°/11 mm. (*hydrochloride*, m.p. 193—194°). Thiophen, conc. HCl, and 40% CH_2O give 40% of 2-thienylmethyl chloride, b.p. 80—81°/18 mm. [with 38% of di-2-thienylmethane, m.p. 45—47°, b.p. 125—126°/9 mm. (lit. 267°)], converted by NH_2Me–EtOH–H_2O at 60° into 2-*thienylmethylmethylamine* (52%), b.p. 75—80°/14 mm. (*hydrochloride*, m.p. 189—190°). 2-Thienyl-Me or Et ketone with $HCO{\cdot}NH_2$ at 180—190° gives form-α-2-thienyl-ethylamide (not isolated) or -n-*propylamide* (I), b.p. 174—178°/12 mm., converted by 30% NaOH at 130° and 100°, respectively, into α-2-*thienyl-ethylamine* (51%), b.p. 83—84°/16 mm. (*hydrochloride*, m.p. 140—142°), and -n-*propylamine*, b.p. 89—91°/13 mm. [*hydrochloride* (II), m.p. 173—175°], respectively. Similar interaction with HCO·NHMe gives α-2-*thienyl-ethyl-* (45%), b.p. 75—76°/10 mm. (*hydrochloride*, m.p. 133—134°), and -n-*propylmethylamine* (27%), b.p. 90—92°/12 mm. (*hydrochloride*, m.p. 121—122°). With HCl–Et_2O, (I) gives a *hydrochloride*, m.p. 234—235° (decomp.), hydrolysed in H_2O, and a little (II). Thiophen with Br–CCl_4 at 0° and later solid NaOH at 100° gives 55% of 2-bromo-(III), b.p. 153—154°, and much 2 : 5-dibromo-thiophen, b.p. 95—98°/16 mm. The Mg derivative (IV) from (III) with $(CH_2)_2O$ in Et_2O at 0° and later C_6H_6 at room temp. gives β-2-thienylethyl alcohol (53%), b.p. 107—109°/14 mm. (*phenylurethane*, m.p. 57—58°), and with propylene oxide in Et_2O gives β-2-thienyl*iso*propyl alcohol (60%), b.p. 106—109°/13 mm. (*phenylurethane*, m.p. 62—63°). With PBr_3 in C_6H_6 or $CHCl_3$, respectively, these give the bromides (*A*), b.p. 98—99°/13 mm. and 98—99°/11 mm., converted by NH_3–EtOH at room temp. into β-2-thienyl-ethylamine (56%), b.p. 88—90°/13 mm. (also obtained from the cyanide by Na–BuOH), and -*isopropylamine*, b.p. 94—96°/15 mm. (*hydrochloride*, m.p. 139—141°), respectively. With NH_2Me–MeOH at 100°, (*A*) give β-2-*thienylethyl-*, b.p. 90—91°/13 mm. (*hydrochloride*, m.p. 154—155°), and β-2-*thienyl*isopropyl-*methylamine*, b.p. 85—88°/14 mm. (*hydrochloride*, m.p. 133—135°). *p*-$C_6H_4Me{\cdot}SO_2{\cdot}[CH_2]_3{\cdot}Cl$ and (IV) in Et_2O at room temp. and later the b.p. give 2-γ-chloro- (61%), b.p. 84—86°/4 mm., converted by NaI in boiling $COMe_2$ into 2-γ-iodo-*n*-propylthiophen, an oil, and thence (as above) γ-2-*thienyl*-n-*propyl-amine* (53%), b.p. 110—112°/19 mm. (*hydrochloride*, m.p. 194—195°), and -*methylamine* (64%), b.p. 112—114°/19 mm. (*hydrochloride*, m.p. 127—128°). Mg β-2-thienylethyl chloride and $(CH_2)_2O$ in Et_2O at room temp. give αβ-*di*-2-*thienylethane* (69%), m.p. 64—65°, b.p. 152—156°/10 mm., and a small fraction, b.p. 100—112°/18 mm. R. S. C.

2 : 3 : 6-Triaminopyridine.—See B., 1942, II, 255.

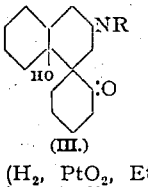
Furoyl- and nicotinoyl-amides.—See B., 1942, II, 272.

Reactions of *N*-dichlorocarbamates. J. Bougault and P. Chabrier (*Compt. rend.*, 1941, **213**, 487—488).—Indole-2-carboxylic acid (I) with $NCl_2{\cdot}OAc$ in AcOH yields 2 : 3 : (5?)-*trichloro*-2 : 3-*epoxy*-2 : 3-*dihydroindole*, m.p. 188°, reduced (Zn dust–AcOH or KI–AcOH) to (5?)-*chloro*-2 : 3-*epoxy*-2 : 3-*dihydroindole*, m.p. 192°. The Me ester of (I) similarly gives *Me* 2 : 3 : (5?)-*trichloro*-3-*hydroxy*-2 : 3-*dihydroindole*-2-*carboxylate*, m.p. 184°, reduced (KI–AcOH) to a *Me dichloro*-3-*hydroxy*-2 : 3-*dihydroindole*-2-*carboxylate*, m.p. 152°. Glycine with $NCl_2{\cdot}CO_2Et$ in H_2O affords $CH_2(NH{\cdot}CO_2Et)_2$, m.p. 130°. W. C. J. R.

Carbazoles.—See B., 1942, III, 172.

Isolation of organic bases.—See A., 1942, II, 248.

Syntheses and reactions of αγ-keto-bases with secondary nitrogen. C. Mannich and O. Hieronimus (*Ber.*, 1942, **75**, [*B*], 49—64).—$CH_2Ph{\cdot}NH_2$,HCl, 40% CH_2O, and *cyclo*hexanone (1 : 1 : 3 mol.) react vigorously when heated together, giving a small proportion of *tert.* base (see later) and, mainly, 2-benzylaminomethyl*cyclo*hexanone (I) [*hydrobromide* (II), m.p. 129°; *oxime*, m.p. 85°; *Bz*, m.p. 134°, and *CO*$_2$*Et-*, b.p. 222°/11 mm., derivative] in ~65% yield. (I) is reduced by Na–Hg in well-cooled, dil. HCl to 2-benzylaminomethyl-*cyclo*hexanol, two forms (*hydrobromide*, m.p. 160—161°, hydrochloride, m.p. 160°, and *Bz* derivative, m.p. 159—161°, of the α-form; *hydrochloride*, m.p. 144°, and *Bz* derivative, m.p. 148°, of the β-form). (II) is successive treatments with KCNO and 10% HCl into 2-*keto*-3-*benzyloctahydroquinazoline*, m.p. 191°, disproportionated by boiling 20% HCl into the corresponding H_{10}-, m.p. 175°, and H_6-compound, m.p. 153° (decomp.) [*hydrochloride*, m.p. 212° (decomp.)]. If in the above reaction the proportion of CH_2O is doubled, the main product is the



(III.)

tert. base (III) (R = CH_2Ph), m.p. 102° (hydrobromide, m.p. 186°; hydrochloride, m.p. 176°; *oxime*, m.p. 186°), reduced (Na–Hg in dil. AcOH) to the $(OH)_2$-base, m.p. 162° (*diacetate*, m.p. 154°). (II), paraformaldehyde, and $COMe_2$ give 10-*hydroxy*-4-*acetyl*-2-*benzyldecahydroisoquinoline* (IV), m.p. 96° (hydrochloride, m.p. 195°; *oxime*, m.p. 131°), reduced (H_2, PtO_2, EtOH) to 10-*hydroxy*-2-*benzyl*-4-*hydroxyethyldecahydroisoquinoline*, m.p. 115—117° (*hydrobromide*, m.p. 240—241°). Conc. H_2SO_4 and (IV) give 4-acetyl-2-benzyloctahydroisoquinoline, base *A* (*perchlorate*, m.p. 146°), and non-cryst. base *B* (*perchlorate*, m.p. 201°). *A* or *B* is rapidly hydrogenated to 4-acetyl-2-benzyldecahydroisoquinoline (*H oxalate*, m.p. 156°). (II), COPhMe, and CH_2O in boiling dioxan afford 10-*hydroxy*-4-*benzoyl*-2-*benzyldecahydroisoquinoline*, m.p. 164°, the hydrochloride, m.p. 214°, of which is also obtained from (I) and $COPh{\cdot}[CH_2]_2{\cdot}Cl$ in boiling EtOH and is converted by conc. H_2SO_4 into 4-*benzoyl*-2-*benzyloctahydroisoquinoline*, m.p. 97°. $CH_2Ph{\cdot}NH_2$,HCl, paraformaldehyde, and $COMe_2$ yield α-benzylaminobutan-γ-one, b.p. 155°/6 mm. [*hydrochloride* (V), m.p. 162°; hydrobromide, m.p. 124—126°; *oxime hydrochloride*, m.p. 151°]. (V) and KCNO afford α-*benzyl*-α-γ-*ketobutylcarbamide*, m.p. 120—121°. (V) is reduced by Na–Hg in dil. HCl to α-benzylaminobutan-γ-ol (VI), b.p. 122—123°/2 mm. (*hydrobromide*, m.p. 57°; N-p-$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}$ derivative, m.p. 236°, and p-*nitrobenzoate hydrochloride*, m.p. 191°). 60% HBr at 160° converts (VI) into γ-bromo-α-benzylaminobutane (*hydrobromide*, m.p. 212°), transformed by $CHNa(CO_2Et)_2$ into α-benzylamino-Δ^{β}-butene, b.p. 95°/12 mm. (*hydrochloride*, m.p. 134—135°), hydrogenated to $NHBu^{\alpha}{\cdot}CH_2Ph$. (V) and paraformaldehyde in boiling $COMe_2$ slowly give two diastereoisomeric forms of 4-hydroxy-5-acetyl-1-benzyl-4-methylpiperidine, which could not be obtained pure or converted into cryst. derivatives but are reduced to a mixture of the corresponding 5-OH·$[CH_2]_2$ bases from which a homogeneous *perchlorate*, m.p. 201°, is isolated in 20% yield; this gives a base, b.p. 223°/12 mm. (*hydrobromide*, m.p. 175°; *diacetate*, m.p. 129—131°). $CH_2Ph{\cdot}NH_2$,HCl, 40% CH_2O, and CHPh:CH·COMe at 100° give a mixture of the very unstable α-benzylamino-δ-benzylidenebutan-γ-one, m.p. 50—51° [*hydrochloride*, m.p. 182—184° (slight decomp.)], reduced to α-*benzylamine*-ε-*phenylpentan*-γ-*ol*, m.p. 87—89° (hydrochloride, m.p. 99—100°), and 4-*hydroxy*-5-*cinnamoyl*-1-*benzyl*-4-*styrylpiperidine*, m.p. 148°. 1-Keto-1 : 2 : 3 : 4-tetrahydronaphthalene, $NH_2Ph{\cdot}NH_2$,HCl, and 40% CH_2O at 100° afford 1-*keto*-2-*benzylaminomethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, m.p. ~160°, converted by KCNO into the *pyrimidine* derivative, $C_{19}H_{18}ON_2$, m.p. 208°, and by $NaNO_2$ into the *NO*-compound, m.p. 94°, which is reduced by Sn and boiling conc. HCl to 2-*benzyltetrahydrobenzindazole hydrochloride*, m.p. 173°. $CH_2Ph{\cdot}NH_2$,HCl, COPhMe, and CH_2O give a mixture of benzylaminopropiophenone (*hydrochloride*, m.p. 163°, converted by KCNO into α-*benzyl*-α-*benzoylethylcarbamide*, m.p. 131°) and 4-*hydroxy*-5-*benzoyl*-4-*phenyl*-1-*benzylpiperidine*, m.p. 116°. 2-*Benzylaminomethyl*cyclo*pentanone hydrochloride*, m.p. 157° (slight decomp.) (whence α-*benzyl*-α-2-*keto*-cyclo*pentylmethylcarbamide*, m.p. 126—127°), is derived from $CH_2Ph{\cdot}NH_2$,HCl, *cyclo*pentanone, and CH_2O. $CH_2O_2{\cdot}C_6H_3{\cdot}CH_2{\cdot}NH_2$, HCl, 40% CH_2O, and *cyclo*hexanone give 2-keto*cyclo*hexylmethyl-3 : 4-methylenedioxybenzylamine [*hydrobromide* (VII), m.p. 155—156°, converted by KCNO into 2-*keto*-3-3′ : 4′-*methylenedioxybenzyl*-*octahydroquinazoline*, m.p. 168°), N-*Bz* compound, m.p. 118°], and the tert. *base* [(cf. (III), R = $CH_2O_2{\cdot}C_6H_3{\cdot}CH_2$], m.p. 167° (hydrobromide, m.p. 250°). 10-*Hydroxy*-4-*acetyl*-2-3′ : 4′-*methylenedioxybenzyldecahydroisoquinoline*, m.p. 127°, is derived from (VII), paraformaldehyde, and $COMe_2$. Methods similar to those described above lead to the following: α-3 : 4-*methylenedioxybenzylamino*-*butan*-γ-*one hydrochloride*, m.p. 176°, 1-*keto*-2-3′ : 4′-*methylenedioxybenzylaminomethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, m.p. 186°, and 2-*keto*-3-3′ : 4′-*methylenedioxybenzylhexahydronaphthapyrimidine*, m.p. 228°; ω-3 : 4-*methylenedioxybenzylaminopropiophenone hydrochloride*, m.p. 187°, and the corresponding *carbamide*, m.p. 144°; α-3 : 4-*methylenedioxybenzylamino*-δ-*benzylidenebutan*-γ-*one hydrochloride*, m.p. ~186° (slight decomp.), hydrogenated to α-3 : 4-methylenedioxybenzylamino-ε-phenylpentan-γ-one (*hydrochloride*, m.p. 205°); 2-3′ : 4′-*methylenedioxybenzylaminomethyl*-cyclo*pentanone hydrochloride*, m.p. 161—162° (slight decomp.), and the corresponding *carbamide*, m.p. 160°; α-*benzylamino*-α-2-*keto*-cyclo*hexyl*-β-*phenylethane hydrochloride*, m.p. 154°. H. W.

5- and 1-Aminobenzo(*f*)quinoline and derivatives. E. R. Barnum and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1942, **64**, 540—542).—2 : 3-$NH_2{\cdot}C_{10}H_6{\cdot}CO_2R$ (R = H or Me), H_3AsO_4, and glycerol at, successively, 120°, 135°, and 145—150° give 5 : 6-*benzoquinoline*-8-*carboxylic acid* (I) (32%), m.p. 204—205°, the *Me* ester (II), m.p. 86°, of which gives the *amide*, m.p. 205—206°. With hot $SOCl_2$ and then

MeOH, (I) gives the *Me* ester (? 7 : 8-)*dichloride*, m.p. 134—135°, converted by NH_3–MeOH at 40—50° into *Me 7-chloro-5 : 6-benzoquinoline-8-carboxylate*, m.p. 187—189°, and by N_2H_4,H_2O in boiling aq. MeOH into *5 : 6-benzoquinoline-8-carboxylhydrazide*, m.p. 203—204° [also obtained from (II)], which yields the *azide*, m.p. 65—67°, and thence (Ac_2O–AcOH) *8-acetamido-*, m.p. 126—127°, and (H_2SO_4 at 0°) *8-amino-5 : 6-benzoquinoline* (III), m.p. 137—138°. With boiling $Br\cdot[CH_2]_n\cdot NEt_2,HBr$–NaOAc–EtOH ($n$ = 2 or 3) or 2-bromopyridine–NaOAc–BuOH–Cu-bronze (trace), this gives *8-β-diethylaminoethyl-*, m.p. 85°, *8-γ-diethylamino-n-propyl-*, an oil (hygroscopic *dihydrochloride*, m.p. 235—240°), and *8-2′-pyridyl-*, m.p. 142—144°, *-amino-5 : 6-benzoquinoline*. 3 : 1-$OH\cdot C_{10}H_6\cdot NH_2,H_2SO_4$ gives, as above, a poor yield of *8-hydroxy-5 : 6-benzoquinoline*, m.p. 104—106°. 5 : 6-Benzocinchoninic acid gives, as above, the *amide*, m.p. 253—255°, *Me*, 104—105°, and *Et* ester, m.p. 56°, and *hydrazide*, m.p. 224—225°, and thence ($NaNO_2$–dil. AcOH; azide in dioxan at 100°) *4-amino-5 : 6-benzoquinoline* (IV), m.p. 149—150° (*Ac*, m.p. 192°, and *p-NMe$_2$·C$_6$H$_4$·CH*: derivative, m.p. 136—138°), and *N-5 : 6-benzocinchoninoyl-N′-diethylaminobenzylidenehydrazide*, m.p. 216—218°. (III), but not (IV), can be diazotised and coupled with R-acid or β-$C_{10}H_7\cdot OH$; (IV) resists alkylation. R. S. C.

N-**Dichlorocarbamates.**—See A., 1942, II, 217.

Benzacridones.—See B., 1942, II, 223.

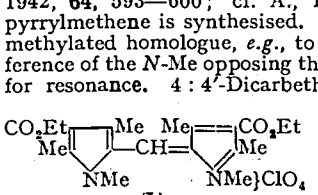
Derivatives of 1′-aza-3 : 4-benzpyrene. M. Weizmann and F. Bograchov (*J.C.S.*, 1942, 377).—3-Aminopyrene and $CH_2Ac\cdot CO_2Et$ in EtOH give *Et β-3-pyrenylaminocrotonate*, m.p. 129°, cyclised in liquid paraffin at 220° to *4′-hydroxy-2′-methyl-1′-aza-3 : 4-benzpyrene*, m.p. 350°, which with PCl_3 affords the *4′-Cl*-compound, m.p. 207°. F. R. S.

Synthesis of some four-membered heterocyclic compounds. T. N. Ghosh and D. Das-Gupta (*J. Indian Chem. Soc.*, 1942, **19**, 41—46).—NH_2Ph and dicarbethoxythioacetocarbamic acid in EtOH give *N-phenyl-NN′-dicarbethoxyvinylenecarbamide* (I), m.p. 74—75° (*Br$_4$*-derivative, m.p. 120—121°), which with N_2H_4 affords *N-phenyl-NN′-(carbethoxycarbohydrazidovinylene)carbamide*, m.p. 171°, remelts 252—253° (decomp.), forming *phenylthiosemicarbazide*, m.p. 188—189° (decomp.), and *CHPh*: derivatives, m.p. 209—210° (decomp.). With NaOEt, (I) is converted into *5-phenyl-1 : 5-diazo-(0,2,2)dicyclo-Δ^3-hexene-2 : 6-dione*, m.p. 245—246°, and when heated at 165—170° is isomerised to *N-phenyl-NN′-dicarbethoxyethenylcarbamide*, m.p. 168—170° (*dianilide*, m.p. 236—238°), which with EtOH–KOH gives the *-carboxy*-derivative, m.p. > 300°. *N-p-Tolyl-NN′-dicarbethoxyvinylenecarbamide*, m.p. 61—62°, is similarly prepared. F. R. S.

Identification of carbonyl compounds by conversion into hydantoins. H. R. Henze and R. J. Speer (*J. Amer. Chem. Soc.*, 1942, **64**, 522—523).—Aldehydes and ketones are identified by conversion into hydantoins by KCN–$(NH_4)_2CO_3$ in 50% EtOH at 58—60°. A few fail to react. The following are described. 4-n-, m.p. 139·5°, and 4-iso-*Butyl-*, m.p. 212·5—216°, 4-n-*amyl-*, m.p. 144·5°, 4-2′-*furyl-*, m.p. 147°, 4-n-*hexyl-*, m.p. 148°, 4-*βζ-dimethyl-Δ^ζ-n-heptenyl-*, m.p. 172—172·5°, 4-*α-ethyl-n-propyl-*, m.p. 175·7—176·1°, 4-p-*tolyl-*, m.p. 182·5°, 4-o-*phenetyl-*, m.p. 185—186°, 4-o-*anisyl-*, m.p. 186—187°, 4-o-*chloro-*, m.p. 176°, 4-3′ : 4′-*dimethoxy-*, m.p. 182·5—183°, 4-3′ : 4′-*methylenedioxy-*, m.p. 207°, 4-m-, m.p. 212°, and 4-p-*hydroxy-*, m.p. 263° (decomp.), 4-p-*dimethylamino-*, m.p. 234—235°, and 4-3′-*methoxy-4′-hydroxy-phenyl-*, m.p. 276° (decomp.), 4-*methyl-*4-n-, m.p. 123—124·5°, and -iso-*propyl-*, m.p. 177°, -n-, m.p. 107·5—108·5°, and -iso-*butyl-*, m.p. 148°, -n-*amyl-*, m.p. 102·5—103·5°, -n-*hexyl-*, m.p. 107·5—108°, *-hydantoin*; 4-p-*tolyl-*, m.p. 203·5°, and 4-p-*anisyl-*, m.p. 210°, *-4-methylhydantoin*; *4-ethyl-4-n-propyl-*, m.p. 144—145°, and -iso*amyl-hydantoin*, m.p. 153°; *4-methyl-5-β-carboxyethyl-*, m.p. 156·5—157·5°, 4-n-*propyl-*4-n-*butyl-*, m.p. 175°, and *4-methyl-4-Δ^α-isobutenyl-hydantoin*, m.p. 194°; 4 : 4-*tetramethylene-*, m.p. 204—205°, *-di*iso*propyl-*, m.p. 207°, -1′-, m.p. 215·5—216°, -2′-, m.p. 268·5—269°, and -3′-*methylpentamethylene-*, m.p. 279—280°, *-hydantoin*; *hydantoins* from carvone, m.p. 193·5—194°, α-hydrindone, m.p. 240°, thujone, m.p. 254·5—255°, and fluorenone, m.p. 324—325° (decomp.). Many other *hydantoins* are listed in American Documentation Document No. 1603. M.p. are corr. R. S. C.

Barbituric acids.—See B., 1942, III, 172.

Pyrrole series. VI. Steric influences on the aromaticity of dipyrrylmethenes. Synthesis and properties of a di-*N*-methyldipyrrylmethene. K. J. Brunnings and A. H. Corwin (*J. Amer. Chem. Soc.*, 1942, **64**, 593—600; cf. A., 1941, II, 338).—A *NN′*-dimethyldipyrrylmethene is synthesised. It is much less stable than the unmethylated homologue, *e.g.*, to Br; this is ascribed to steric interference of the *N*-Me opposing the planar alignment of rings necessary for resonance. 4 : 4′-Dicarbethoxy-1 : 3 : 5 : 1′ : 3′ : 5′-hexamethyldi-2-pyrrylmethene perchlorate (I), decomp. 160—170° (explosive), is obtained from (*a*) 4 : 4′-dicarbethoxy-1 : 3 : 5 : 1′ : 3′ : 5′-hexamethyldi-2-pyrrylmethane (II) by, best (50% yield), 1 mol. of Br in CCl_4, (*b*) 3-carbethoxy-1 : 2 : 4-trimethylpyrrole (III) (best, 2 mols.; 73% yield), 2-formyl-4-carbethoxy-1 : 3 : 5-trimethylpyrrole (IV), and gaseous HCl in CCl_4, and (*c*) (III) and 98% HCO_2H in conc. aq. HCl–Et_2O, best (54% yield) at 50°. The structure of (I) is proved by hydrogenation (Pd–C) in MeOH to (II) and conversion by 2·5% KOH–MeOH at room temp. into 4 : 4′-*dicarbethoxy*-1 : 3 : 5 : 1′ : 3′ : 5′-*hexamethyldi-2-pyrrylcarbinyl Me ether*, $CHR_2\cdot OMe$ (R = substituted pyrryl group) (82%), m.p. 113—114°, whence (I) (80—85%) is regenerated by HCl–Et_2O or –hexane and later $HClO_4$. The bromide solution intermediate in method (*a*) above with 2·5% aq. NaOH gives 4 : 4′-*dicarbethoxy*-1 : 3 : 5 : 1′ : 3′ : 5′-*hexamethyldi-2-pyrrylcarbinol* (V) (42%), m.p. 142—143°. The chloride and bromide corresponding with (I) are red oils, sol. in dil. acid to solutions which gradually decompose. Treatment of the chloride at p_H 1·5—2 with NaOH to give p_H 3·5—4 decolorises the red solution and 88% of (V) is gradually deposited; the same reaction is caused at p_H 1·5 by adding NaF. All these reactions indicate ready transformation of the methene salts into the covalent forms, *e.g.*, CHR_2Br, and show the great effect of the anion on the ease of the change. The absorption spectrum of (I) (max. at 4700 A., log E ~1·1) differs only as expected from that of the 3 : 5 : 3′ : 5′-Me_4 homologue (max. at 5100 A., log E ~1·9; narrower band) (both $1·3 \times 10^{-5}$M. in $CHCl_3$). Use of 2 mols. of Br in method (*a*) above gives only (IV) and *2-bromo-4-carbethoxy*-1 : 3 : 5-*trimethylpyrrole* (VI), m.p. 57—58°, which are also obtained from the methene bromide and Br in CCl_4 or H_2O. (IV) is also obtained from the mother-liquor from (I) in method (*a*). This decomp. probably proceeds by cleavage of the bromide to the 5-$CHBr_2$ compound + (III), hydrolysis of the former product, and bromination of the latter (realised in a separate experiment: product, m.p. 54—55°, decomp. 145—150°). R. S. C.



(I.)

Pyrimidines. CLXXVI. Action of keten on 5 : 5-dibromohydroxyhydrouracil. M. Fytelson and T. B. Johnson (*J. Amer. Chem. Soc.*, 1942, **64**, 306—308).—Keten does not react with hydrouracil, uracils, or 5 : 5-dibromo-4-hydroxyhydrouracil (I) at room temp. In boiling $COMe_2$, (I) and kcten give 5-bromouracil (II) or alone at 90—95° gives (II) and some ? impure $CH_2Br\cdot CO_2H$. In presence of SiO_2 gel at 90°, (I) and keten give *5-bromo-3-acetyluracil* (III), m.p. 175·5—177° [in HCl gives (II)], (II), and $COMe\cdot CH_2Br$ [formed by decomp. of (III) to (II) and HOBr, followed by addition of HOBr to diketen]; after partial interaction at 60°, (III), $COMe\cdot CH_2Br$, and $CH_2Br\cdot CO_2H$ are obtained. With Ac_2O at room temp., (I) gives the *O-acetate*, m.p. 146—148°. In presence of SiO_2 gel at 100° or 80°, 5 : 5-dibromo-4-hydroxy-4-methylhydrouracil gives 5-bromo-4-methyluracil, m.p. 226—230° (decomp.). R. S. C.

Chemotherapy. IV. Sulphanilamidopyrimidines. R. O. Roblin, jun., P. S. Winnek, and J. P. English (*J. Amer. Chem. Soc.*, 1942, **64**, 567—570; cf. A., 1941, II, 288).—Pharmacological activity (*A* = active, *S* = slightly active, *I* = inactive), solubility in H_2O, and max. blood level are recorded for *2-sulphanilamido-4-methoxy-* (*A*), m.p. 241—242°, *-4-ethoxy-* (*S*), m.p. 255—256°, and -4 : 6-dimethyl- (I) (*A*), m.p. 198—199° (lit. 178—180°) [Ac derivative, m.p. 249—250° (lit. 246·8—247·4°)], *5-chloro-2-sulphanilamido-* (*S*), m.p. 246—247°, *4-sulphanilamido-2-methyl-* (*S*), m.p. 207—208°, *5-sulphanilamido-* (II) (*A*), m.p. 260—261°, *2-chloro-5-sulphanilamido-* (*S*), m.p. 206—207°, *2-amino-5-sulphanilamido-* (*S*), m.p. 293—298°, *5-sulphanilamido-2-methoxy-* (*A*), m.p. 232—234°, and 2 : 5-*disulphanilamido-* (*I*), m.p. 231—232°, *-pyrimidine* and other derivatives (A., 1940, II, 359). 4-Sulphanilamidopyrimidine, inactive *in vitro*, is active *in vivo*, possibly by hydrolysis, which is facile. Only (I) is as active as sulphadiazine (the 2-$SO_2\cdot NH_2$-derivative). Activity and max. blood level do not always parallel solubility in H_2O. The Na salt, anhyd. and $+2H_2O$ (prep. by NaOH–EtOH on the 5-nitro-2-amino-compound at 70—75°), of 5-nitro-2-hydroxypyrimidine with $POCl_3$, finally at the b.p., gives *2-chloro-5-nitropyrimidine* (II), m.p. 110—111°. With boiling NaOMe–MeOH, (II) gives 5-nitro- and thence (H_2–Pd; MeOH; 50 lb.) 5-amino-2-methoxypyrimidine. With Fe in 1·5% aq. AcOH, (II) gives *2-chloro-5-amino-*, m.p. 198—199° (decomp.), reduced by H_2–Pd–$CaCO_3$ and BaO in MeOH at 25°/60 lb. to *5-amino-pyrimidine* (III), m.p. 170—171°. 4-Chloro-2-amino- with boiling NaOEt–EtOH gives *2-amino-4-ethoxypyrimidine*, m.p. 154—156°. *5-Chloro-2-amino-*, m.p. 234—236° (sealed tube), and 5-nitro-2-acetamido-pyridine, m.p. 187—188° (decomp.) (lit. 172°), are also recorded. (II) is not obtained from $NO_2\cdot CH(CHO)_2$ and $NH{:}CH\cdot NH_2$ and is not hydrogenated directly to (III). M.p. are corr. R. S. C.

Dicyclic compounds and their analogy with naphthalene. VI. Indazole series. K. Fries, K. Fabel, and H. Eckhardt (*Annalen*, 1941, **550**, 31—49; cf. A., 1937, II, 124).—The general behaviour of indazole and many of its derivatives shows that it belongs to the naphthoid dicyclic series. The slight divergencies from the substitution regularities characteristic of this series are ascribed to the influence of NH of the hetero-ring. The solid diazonium sulphate from 5-amino-1 : 3-diphenylindazole is converted by warming with a mixture of AcOH and conc. H_2SO_4 into *5-hydroxy-1 : 3-diphenylindazole*, m.p. 196° (*acetate*, m.p. 82°), converted by Br in AcOH into *4-bromo-5-hydroxy-1 : 3-diphenylindazole* (I), m.p. 146°; this by further treatment with Br in AcOH gives a keto-bromide, reduced by $SnCl_2$ in AcOH to (I) and hydrolysed by H_2O to 1 : 3-*diphenyl-4 : 5-indazolequinone*, m.p. ~208° after becoming black (*quinoxaline*

derivative, $C_{25}H_{16}N_4$, m.p. 165° and, after re-solidification, m.p. 185°). HNO_3 (*d* 1·52) and conc. H_2SO_4 at 10° convert 6-nitro- into 5 : 6-*dinitro-indazole*, m.p. 224° (after decomp.), reduced by $SnCl_2$ and conc. HCl to 5 : 6-*diaminoindazole* (**II**), m.p. 275° after decomp. at ~265°, which with HNO_2 affords 1 : 2 : 3-*triazoloindazole*, decomp. >300° after blackening at ~280°. (**II**) is converted by 2N-HCl at 170—180° into 5 : 6-*dihydroxyindazole* (**III**), m.p. 235° (*diacetate*, m.p. 143°), transformed by Br in AcOH into 4 : 7-dibromo-5 : 6-dihydroxyindazole (**IV**), m.p. 184° (decomp.) [*hydrobromide*, m.p. ~200° (decomp.); Ac_3 derivative, m.p. 162°]. Attempts to oxidise (**III**) or (**IV**) to an *o*-quinone were unsuccessful. Chlorination of (**II**) or (**III**) in sunlight gives 7 : 7-*dichloro*-4 : 5 : 6-*triketo*-4 : 5 : 6 : 7-*tetrahydroindazole dihydrate*, m.p. 170° (decomp.), also obtained by chlorination of (**III**) and converted by NaOAc followed by acid into 5 : 6-*dihydroxy*-4 : 7-*indazolequinone* (**V**), m.p. 330° to a dark melt after decomp. at 290°, and reduced by $SnCl_2$ and conc. HCl to 4 : 5 : 6 : 7-*tetrahydroxyindazole* (**VI**) [*hydrochloride* (**VII**), m.p. ~225° (decomp.); *tetra-acetate*, m.p. 181°]. (**VII**) when dissolved in H_2O passes into (**V**) and is oxidised by HNO_3 (*d* 1·52) in AcOH to 4 : 5 : 6 : 7-tetraketo-4 : 5 : 6 : 7-tetrahydroindazole. Hot, fuming, HNO_3 oxidises (**VI**) to pyrazole-4 : 5-dicarboxylic acid, which could not be converted into an internal anhydride. When heated alone it gives pyrazole-4-carboxylic acid, m.p. 275°, whilst with Ac_2O it affords the N-*Ac* derivative, m.p. 169°, which is transformed ($SOCl_2$) through the dichloride into *pyrazole*-4 : 5-*dicarboxanilide*, m.p. 244°. Indazole is scarcely hydrogenated in presence of Pd–$BaSO_4$ in AcOH or of Ni-Co–Cu in EtOH at 20°/100 atm. or at 130° but in presence of much Pt it gives 4 : 5 : 6 : 7-tetrahydroindazole. 1-Methylindazole is slowly reduced to the non-cryst. tetrahydride (*picrate*, m.p. 148°) but the 2-Me compound is much more rapidly and similarly reduced. The behaviour of an equimol. mixture of C_6H_6 and $C_{10}H_8$ shows that $C_{10}H_8$ is much the more rapidly hydrogenated (Pt–AcOH). 5-Aminoindazole with PhN_2Cl gives 5-*amino*-4-*benzeneazoindazole*, m.p. 164°, reduced by $SnCl_2$ to 4 : 5-*diaminoindazole*, m.p. 181°, which affords a *quinoxaline* derivative, $C_{21}H_{14}N_2$, m.p. 257°. 5-*Amino*-4-*benzeneazo*-1-, m.p. 202°, and -2-, a viscous mass [*hydrochloride*, m.p. 237° (decomp.)], -*methylindazole* are obtained similarly whereas the corresponding *diazoamino*-compounds have m.p. 125° and 176° (decomp.), respectively. 6-, m.p. 196°, and 5-, m.p. 155° after sotening at 145°, -*benzylideneaminoindazole* are readily converted into *dihydroacridone* derivatives, $C_{20}H_{15}N_5$, both of m.p. >360°.

H. W.

Cinnolines. I. New examples. J. C. E. Simpson and O. Stephenson (*J.C.S.*, 1942, 353—358).—*Phenyl*-(5-*bromo*-2-*aminophenyl*)-*methylcarbinol*, m.p. 100° (N-*Ac*, m.p. 181—182°, and N-*Bz* derivatives, m.p. 196°), prepared from $COPh{\cdot}C_6H_3Br{\cdot}NH_2$-5 : 2 and MgMeI, is dehydrated (H_2SO_4) to α-*phenyl*-α-(5-*bromo*-2-*benzamidophenyl*)*ethylene*, m.p. 113·5—114° [*sulphates* (+$2H_2O$), m.p. 107° and 154°], which with HNO_2 affords 6-*bromo*-4-*phenylcinnoline*, m.p. 143·5—144·5°. Reduction (Fe–AcOH) of the anthroxan (**I**) from o-$NO_2{\cdot}C_6H_4{\cdot}OH$ and PhOH gives 2 : 5-$NH_2{\cdot}C_6H_3Cl{\cdot}CO{\cdot}C_6H_4{\cdot}OH$-4′ (**II**) (*Bz*$_2$ derivative, m.p. 143°), deaminated to 3-$C_6H_4Cl{\cdot}CO{\cdot}C_6H_4{\cdot}OH$-4′, m.p. 169·5—171° (lit. m.p. 161°), and converted (HNO_2–CuCl) into 2 : 5-*dichloro*-4′-*hydroxybenzophenone*, m.p. 171—172·5° (under different conditions, a *substance*, m.p. 224—226°, is obtained), which is oxidised ($KMnO_4$) to 2 : 5-$C_6H_3Cl_2{\cdot}CO_2H$ (*m*-*nitroanilide*, m.p. 151—152°). Na–MeOH and (**I**) give the *chloro*-*methoxyanthroxan*, m.p. 143—145°, reduced (Fe–AcOH) to 5-*chloro*-2-*amino*-4′-*methoxybenzophenone*, m.p. 100—101°. MgMeI and (**II**) yield, after decomp., α-(5-*chloro*-2-*aminophenyl*)-α-(4′-*hydroxyphenyl*)*ethylene*, m.p. 159° (*Bz*$_2$ derivative, m.p. 130·5—132°), which with HCl–$NaNO_2$ gives 6-*chloro*-4-(4′-*hydroxyphenyl*)-*cinnoline*, m.p. 257—259° (decomp.) (*Bz* derivative, m.p. 156°). The anthroxan from *p*-cresol and o-$NO_2{\cdot}C_6H_4{\cdot}CHO$ is reduced to 2 : 5-$NH_2{\cdot}C_6H_3Cl{\cdot}CO{\cdot}C_6H_3Me{\cdot}OH$-5′ : 2′ (**III**) (*Bz*$_2$ derivative, m.p. 156—157°), which is converted into the 2 : 5-*Cl*$_2$-compound, m.p. 149—150°. This anthroxan with Na–MeOH yields the *methoxyanthroxan*, m.p. 96—98°, which is reduced (Fe–AcOH) to 5-*chloro*-2-*amino*-2′-*methoxy*-5′-*methylbenzophenone*, m.p. 100—101° (N-*Ac* derivative, m.p. 136—137°). MgMeI and (**III**) give a resin, converted through the *hydrochloride*, m.p. 222—223° (decomp.), into α-(5-*chloro*-2-*aminophenyl*)-α-(2′-*hydroxy*-5′-*methylphenyl*)*ethylene*, m.p. 108° [*Bz*$_2$ derivative, m.p. 119°; *Bz*$_3$ (?) derivative, m.p. 235°], which with HCl–$NaNO_2$ affords 6-*chloro*-4-(2′-*hydroxy*-5′-*methylphenyl*)*cinnoline*, m.p. 260—261° (decomp.) (*Bz* derivative, m.p. 140°).

F. R. S.

Pyridylquinolines.—See B., 1942, II, 255.

Alkaline hydrolysis of fluorenone*spiro*hydantoin. W. H. McCown with H. R. Henze (*J. Amer. Chem. Soc.*, 1942, **64**, 689—690).—Fluorenone*spiro*hydantoin (**I**), m.p. 324—325° (decomp.) (lit. 308—310°), is obtained in 78% yield from fluorenone, KCN, and $(NH_4)_2CO_3$ at 110°. In ~50% aq. $Ba(OH)_2$ at 110—120° it gives 9-*amino*-9-*carbamylfluorene* (**I**) (80%), m.p. 254—256° (decomp.; sealed tube), and some fluorenone. In HCl–EtOH at 120°, (**I**) gives 9-chlorofluorene, m.p. 91—92°, and with boiling NH_2Ph gives NH_3 and 9-*aminofluorene*-9-*carboxylanilide*, m.p. 292—297° (decomp.). 9-Hydroxyfluorene-9-carboxylic acid (prep. from phenanthraquinone by 20% NaOH at 100°; 42% yield), new m.p. 167—168°, with PCl_5 at 0° gives 9-chlorofluorene-9-carboxyl chloride (30%), m.p. 111°, converted by NH_3–Et_2O into the amide, which with $NaNH_2$–NH_3 gives an amorphous product, m.p. 60—70° (decomp.). M.p. are corr.

R. S. C.

Technics in the synthesis of porphyrindin. H. A. Lillevik, R. L. Hossfeld, H. V. Lindstrom, R. T. Arnold, and R. A. Gortner (*J. Org. Chem.*, 1942, **7**, 164—168).—The prep. of porphyrindin from $CMe_2{:}N{\cdot}OH$ (**I**) is described. The yield of $OH{\cdot}NH{\cdot}CMe_2{\cdot}CN$ (**II**) from (**I**) is improved by cold room technique and by extractions with light petroleum instead of crystallisation. The most difficult step [conversion of (**II**) into $OH{\cdot}NH{\cdot}CMe_2{\cdot}C(OEt){:}NH,2HCl$] gives good yields under anhyd. conditions.

H. W.

Chlorophyll. CXI. Purpurins. 10-Hydroxymesophæophorbide *a* and its direct transformation into mesopurpurin 7. M. Strell (*Annalen*, 1941, **550**, 50—66).—Oxidation of mesophæophorbide with $KMnO_4$ in C_5H_5N (cf. Fischer and Kahr, A., 1937, II, 470), removal of the " unstable chlorin," and treatment of the residue with CH_2N_2 leads to 10-*hydroxymethylmesophæophorbide* (**I**), m.p. 255°, $[\alpha]^{20}$ —348° in $COMe_2$, isomerised by HI in AcOH at 100° to 10-hydroxyphæoporphyrin a_5 (**II**), m.p. 270°, identified by spectrum, mixed m.p., and transformation into phæoporphyrin a_7. Oxidation of cryst. phæophorbide (cf. *loc. cit.*) and further treatment of the product described above gives a flocky hydroxyphorbide which softens at 265° but does not melt completely. The mixed m.p. with a material obtained by hydrolysis of 10-acetoxymethylphæophorbide (**III**) shows the same phenomenon. The spectrum is identical with that of (**III**). Addition of $CHN_2{\cdot}CO_2Et$ causes slight displacement towards blue. Isomerisation by HI leads to 10-hydroxyphæoporphyrin a_6. Oxidation of mesomethylphæophorbide by $KMnO_4$ gives (**I**) and " *unstable mesochlorin* 7 " *Me*$_2$ *ester*, non-cryst., m.p. 225°. Although fully esterified this substance can be removed from Et_2O by dil. NaOH but not by dil. NH_3, thus giving further evidence of the lactonic nature of the compound. It is esterified by CH_2N_2 quantitatively to mesopurpurin 7. Catalytic hydrogenation of (**I**) in $COMe_2$ gives unchanged material and its leuco-compound whilst the product obtained in AcOH is re-oxidised to (**II**). The tendency towards passage into the porphyrin system exceeds that of reduction of OH. (**I**) is very stable towards protracted boiling in C_5H_5N. Treatment of (**I**) with MeOH–Na_2CO_3 quickly leads through a red-violet to a red solution which ultimately becomes green and then contains almost exclusively mesorhodochlorin, identified spectroscopically and by isomerisation (HI) to rhodoporphyrin. The red stage is due to the presence of *mesopropurpurin* 7 (**IV**). Pptn. of the Et_2O solution with MeOH gives mesopurpurin 7 (**V**), also obtained in poor yield when the Et_2O solution is exposed to air and almost quantitatively by oxidation with $FeCl_3$–MeOH. If methanolysis is effected in presence of O_2, (**IV**) is not formed and (**V**) is obtained directly. (**IV**) is also produced during the catalytic hydrogenation of (**V**) in dioxan. Tentatively (**IV**) is regarded as a γ-glycollic acid. The propurpurin reaction is shown by 10-acetoxy- and 10-hydroxymethyl-phæophorbide but scarcely by methylphæophorbide and appears to be the best criterion of allomerised phæophorbide. Methanolysis by CH_2N_2–MeOH gives similar results. When shaken with 10% KOH–MeOH for 3 hr. (**I**) yields " unstable mesochlorin 7 " whereas after very short action with much more dil. alkali the presence of (**IV**) in small amount is established. The *Cu*, m.p. 245°, and *Zn*, m.p. 220°, complex salts of purpurin 7 Me_3 ester are described.

H. W.

Structure of imidoporphyrin in relation to phthalocyanines. F. Endermann (*Z. physikal. Chem.*, 1942, **A**, **190**, 129—173).—The structure of these compounds is discussed and formulæ are proposed.

C. R. H.

***N*-β-Morpholinoethyl furoate and tetrahydrofuroate.**—See B., 1942, 11, 261.

Isosteric and structurally similar compounds. XV. Thiazole-5-carboxylamide. H. Erlenmeyer, E. Schmid, and A. Kleiber (*Helv. Chim. Acta*, 1942, **25**, 375—376).—*Thiazole*-5-*carboxylamide*, m.p. 196°, is obtained from conc. NH_3 and the acid chloride or from Et thiazole-5-carboxylate and NH_3–EtOH at room temp. It does not form mixed crystals with nicotinamide.

H. W.

Structural chemical investigations. V. *cyclo*Hexenothiazole. H. Erlenmeyer and M. Simon (*Helv. Chim. Acta*, 1942, **25**, 362—364).—2-Bromo*cyclo*hexanone slowly condenses with $HCS{\cdot}NH_2$ in Et_2O to cyclo*hexenothiazole*, b.p. 126—127°/22 mm. (*picrate*, m.p. 183—184°; hygroscopic hydrochloride and hydrobromide; oxalate, m.p. 112°), which resembles quinoline in its power of forming sparingly sol. metallic complexes. Similarly $MeCS{\cdot}NH_2$ yields 2-*methyl*cyclo*hexenothiazole*, b.p. 146—148°/22 mm. (*picrate*, m.p. 123—124°), which readily forms metallic complexes and condenses with *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ in presence of anhyd. $ZnCl_2$ to 2-*p*-*dimethylaminostyryl*cyclo*hexenothiazole*, m.p. >190° (decomp.). 2-*Thiol*cyclo*hexenothiazole*, m.p. 176°, gives sparingly sol. Cd^{II}, Cu^{II}, and Ag^{I} salts.

H. W.

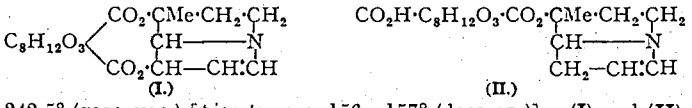
Benzthiazoles.—See B., 1942, II, 223.

Action of chlorine on arylthiocarbimides and reactions of aryl *iso*cyanodichlorides. III. Addition of chlorine to α-naphthylthioearb-

imide and the structure of the compounds obtained. G. M. Dyson and T. Harrington (*J.C.S.*, 1942, 374—375; cf. A., 1942, II, 169).—α-$C_{10}H_7$·NCS (I) and Cl_2–$CHCl_3$ give an unstable additive compound, converted in air into *bis-(α-naphthylthiocarbimide) oxide*, m.p. 80°. Further addition of Cl_2 produces 2 : 4′-*dichloronaphtha*(1′ : 2′ : 4 : 5)-*thiazole*, m.p. 113°, also obtained by chlorination of 4-*chloro-α-naphthylthiocarbimide*, m.p. 87°. Prolonged chlorination of (I) yields a *compound*, $C_{11}H_2NCl_5S$. A. T. P.

VII.—ALKALOIDS.

Alkaloid of *Crotolaria Grantiana*. I. Grantianine. R. Adams, M. Carmack, and E. F. Rogers (*J. Amer. Chem. Soc.*, 1942, **64**, 571—573).—The seeds of this plant yield to 95% EtOH at room temp. *grantianine* (I), $C_{18}H_{23}O_7N$, m.p. 204—205° (decomp.), $[\alpha]_D^{27}$ +50·6° in $CHCl_3$ [*methiodide*, m.p. 242—243° (vac.); *picrate*, m.p. 225—228° (decomp. from ~210—215°); hydrochloride, m.p. 221—222° (decomp.; vac.)], hydrolysed by hot KOH–MeOH to retronecine (44%) and hydrogenated (PtO_2–EtOH–AcOH) to a H_4-derivative (II), m.p.

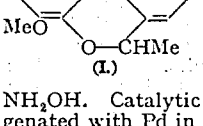


242·5° (gas; vac.) [*picrate*, m.p. 156—157° (decomp.)]. (I) and (II) probably have the structure shown; the acidic component, grantianinic acid, $C_8H_{12}O_3(CO_2H)_2$, may be a CH_2·CO_2H derivative of monocrotalic acid. M.p. are corr. R. S. C.

Alkaloids of papaveraceous plants. XXXII. *Stylophorum diphyllum* (Michx.), Nutt., *Dicranostigma franchetianum* (Prain), Fedde, and *Glaucium serpieri*, Heldr. XXXIII. *Corydalis cheilanthefolia*, Hemsl. R. H. F. Manske (*Canad. J. Res.*, 1942, **20**, **B**, 53—56, 57—60).—XXXII. *S diphyllum* and *D. franchetianum* contain protopine (I) (~0·03%), chelidonine (0·05, 0·02%, respectively), and *l*- + *dl*-stylopine (II), and their separate generic rank is chemically unjustified. *G. serpieri* contains glaucine, *iso*corydine (0·004%), (I), aurotensine (0·002%), and an amorphous base (? cheilanthifoline or an isomeride) which with CH_2N_2 gives partly racemised sinactine.

XXXIII. *C. cheilantheifolia* contains *l*-canadine, berberine, (II), *l*-corypalmine, *l*-cheilanthifoline (0·0002%), (I) (0·14% from the aerial parts; 0·74% from the roots), *allo*cryptopine (0·06%), and a neutral nitrogenous *compound*, m.p. > 360°. The structure of ophiocarpine is confirmed by oxidation by $KMnO_4$ to 1-keto-6 : 7-methylenedioxy-1 : 2 : 3 : 4-tetrahydro*iso*quinoline. R. S. C.

New degradation product from morphine. L. Small (*J. Org. Chem.*, 1942, **7**, 158—163).—3-*Methoxy-5-methyl-5-phenanthro*[4 : 5-bcd]-*pyran* (I), m.p. 118·5°, $[\alpha]_D^{25}$ ±0·0° in EtOH (*picrate*, m.p. 107—108°), is isolated from the residues from the purification of methylmorphenol prepared by the degradation of morphine according to Mosettig *et al.* (A., 1935, 366).



(I) is not sol. in aq. or alcoholic alkali, gives no colour with $FeCl_3$, and does not react with NH_2OH. Catalytic hydrogenation is negative and it is not dehydrogenated with Pd in boiling $C_{10}H_8$. It is not oxidised by $KMnO_4$ in boiling $COMe_2$ and yields a non-cryst. product with CrO_3. With Br in glacial AcOH (I) gives a Br_1-derivative, m.p. 104—105°. With boiling 48% HBr (I) gives a transient, intense purple colour but appears otherwise unchanged. With boiling Ac_2O–HI (*d* 1·7) (I) gives a *compound*, $C_{16}H_{12}O_2$, m.p. 84—84·5°. Distillation of (I) with Zn dust gives pyrene. In addition to (I) the isolation of a *liquid* (C 80·23, H 10·42%) and a cryst. N-free *solid*, m.p. 270—272° (slight decomp.; becomes yellow at 265°), $[\alpha]_D^{20}$ ±0·0° in dioxan, is described. Thebenol (II) could not be converted into (I) since (II) is unchanged by NH_3–$(NH_4)_2SO_3$ at 140° and converted into a black tar by NaOAc, NH_4Cl, and AcOH at 270°. The pyran ring of (II) could not be opened. Attempts to resolve (II) were unsuccessful. H. W.

***Thalictrum foliolosum*, DC. Isolation and characterisation of a new alkaloid thalictrine.** S. K. Vashistha and S. Siddiqui (*J. Indian Chem. Soc.*, 1941, **18**, 641—645).—The rhizome contains berberine and *thalictrine*, $C_{20}H_{27}O_4N$, m.p. 208°, a quaternary hydroxide containing $(OMe)_2$, NMe, phenolic OH, and two double bonds [*chloride*, softens 161°, frothes 163—165°; *chloroplatinate*, darkens 215°, swells 231°, decomp. 233—234°; *iodide*, m.p. 265° (decomp.); *picrate*, m.p. 207—208°; *tetrabromide acetate*, blackens 200°, decomp. 248—250°]. F. R. G.

Argentine plants. IV. Alkaloids from *Erythrina* species. R. A. Gentile and R. Labriola (*J. Org. Chem.*, 1942, **7**, 136—139).—The isolation of hypaphorine (I), erysodine (II), m.p. 204—205°, $[\alpha]_D$ +250° in EtOH, erysopine (III), m.p. 241°, $[\alpha]_D$ +265° in EtOH–glycerol, and erysovine (IV), m.p. 175—176°, from *E. crista galli* is described. *E. falcata* yields (I), (II), (III), erysocine, m.p. 160—161°, $[\alpha]_D$ +236·4° in EtOH, and (IV) whilst (I), (II), (III), and (IV) are obtained from *E. dominguezzii*. H. W.

Koto-tsuzurafuji alkaloids.—See B., 1942, 111, 172.

VIII.—ORGANO-METALLIC COMPOUNDS.

Preparation and properties of dimethylphosphine. N. Davidson and H. C. Brown (*J. Amer. Chem. Soc.*, 1942, **64**, 718).—Prep. of $PHMe_2$ from PH_4I, ZnO, and MeI at 100° (Hofmann, 1871) is modernised. The v.p. is given by $\log p = -1370/T + 7{\cdot}539$, whence are calc. b.p. 21·1°, ΔH (vapour) 6·27 kg.-cal., and Trouton's const. 21·2. R. S. C.

IX.—PROTEINS.

Recent advances in protein chemistry. S. Moore (*Wallerstein Lab. Comm.*, 1942, **5**, 27—34).—The discussion relates to mol. wt., analysis of hydrolysates (solubility product and isotope dilution methods), and *in vivo* equilibria. I. A. P.

Denaturation of edestan by acid: T. B. Osborne's edestan. K. Bailey (*Biochem. J.*, 1942, **36**, 140—154).—The kinetics of HCl-denaturation of edestin (I) to edestan (II) are recorded at various p_H. The initial reaction is rapid at p_H below 4, but becomes slower, partly because of a rise in p_H. (II) is a monodispserse fragmentation product of (I). Edestin chloride freshly pptd. from aq. NaCl has the same *X*-ray diffraction pattern as (I), but after removal of NaCl it changes to one typical of denatured proteins. The no. of SH groups ∝ the amount of (II), in which it represents ~¼ of the cystine-S. Total N and tryptophan are lower in (II) than in (I), the fall in total N being mainly due to hydration of the mol. There is a small loss of sol. N as NH_3 and tryptophan. R. L. E.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Resins. VI. Determination of *d*-pimaric acid in mixtures of native resin acids. W. Sandermann (*Ber.*, 1942, **75**, [*B*], 174—178).—The mixture of acids is isomerised by boiling with AcOH for 2 hr., after which only *d*-pimaric (I) and abietic acid (II) are present. The final val. $([\alpha]_D)_e$ of the sp. rotation is determined. % (I) = $\{([\alpha]_D)_e + 8\} \times 100/138$. The method is not valid for colophony. (II) has $[\alpha]_D$ −103·5° in Et_2O, −81·0° in AcOH, −103° in dioxan, −12·5° in C_6H_6, and −70° to −79° in *cyclo*hexane whereas (I) has +70° in Et_2O, +75° in $CHCl_3$, +75° in C_6H_6 and +57° in AcOH. H. W.

Purification of penicillin. E. P. Abraham and E. Chain (*Nature*, 1942, **149**, 328).—Penicillin (I) has been obtained in the form of a highly purified Ba salt by extraction from amyl acetate into H_2O, chromatography (Al_2O_3), treatment of the active fraction with Al-Hg, and finally repeated chromatography. Its activity is 450—500 Oxford (I) units per mg. A. A. E.

Nitrogenous character of penicillin. E. P. Abraham, W. Baker, E. Chain, H. W. Florey, E. R. Holiday, and R. Robinson (*Nature*, 1942, **149**, 356).—Analysis of the Ba salt of penicillin (I) (cf. preceding abstract) corresponds with $C_{24}H_{32}O_{10}N_2Ba$. The salt is lævorotatory (H_2O); the absorption spectrum does not suggest the presence of aromatic rings. A. A. E.

XI.—ANALYSIS.

Rapid chromic-nesslerisation determination of nitrogen in biological materials.—See A., 1942, III, 503.

Micro-analytical determination of sulphur in organic compounds by catalytic hydrogenation. K. Bürger (*Angew. Chem.*, 1941, **54**, 392—394).—A modified method is described. A. T. P.

Determination of glycerol, ethylene glycol, and propylene αβ-glycol in presence of one another. G. Hoepe and W. D. Treadwell (*Helv. Chim. Acta*, 1942, **25**, 353—361).—The mixture, dissolved in H_2O, is oxidised by KIO_4 at room temp. and HCO_2H is determined in one portion of the solution by titration with 0·1N-NaOH using Me-red as indicator [OH·CH(CH_2·OH)$_2$ (I) + $2KIO_4$ = $2CH_2O$ + HCO_2H + $2KIO_3$ + H_2O]. In a second portion the total aldehyde is determined by addition of Na_2SO_3 and titration of NaOH formed by 0·1N-HCl in presence of thymolphthalein [$(CH_2$·OH)$_2$ (II) + KIO_4 = $2CH_2O$ + KIO_3 + H_2O; OH·CHMe·CH_2·OH (III) + KIO_4 = CH_2O + MeCHO + KIO_3 + H_2O]. CH_2O is determined by successive addition of 0·1N-KCN, HNO_3, and 0·1N-$AgNO_3$ and titration of excess of the latter by NH_4CNS; residual KIO_3 and KIO_4 are determined in a blank experiment. The amount of MeCHO formed is a measure of (III) whilst (II) is determined from CH_2O after deduction of the amounts due to (I) and (III). H. W.

Identification of carbonyl compounds.—See A., 1942, II, 271.

Action of vanadous sulphate on organic compounds.—See A., 1942, I, 279.

Colorimetric determination of cyclic ketones in solvent mixtures. G. Zeidler and H. Kreis (*Angew. Chem.*, 1941, **54**, 360—361).—The Lange colorimeter is used after interaction of the product with *o*-NO_2·C_6H_4·CHO–aq. PhOH. A. T. P.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

SEPTEMBER, 1942.

I.—ALIPHATIC.

Strength of carbon–hydrogen and carbon–carbon bonds. Carbon–hydrogen bond strengths in methane and ethane.—See A., 1942, I, 258.

Catalytic polymerisation of olefines in presence of phosphoric acid.—See A., 1942, I, 302.

Manufacture of butadiene.—See B., 1942, II, 211.

Gaseous hydrogenation and polymerisation reactions.—See A., 1942, I, 301.

Thermal reaction of ethylene with acetylene.—See B., 1942, II, 209.

Preparation of alkyl halides.—See B., 1942, II, 212.

Chlorination of methane.—See B., 1942, II, 209.

Reactions of bromine with carbon tetrachloride and tetrachloroethylene following neutron capture and isomeric nuclear transition.—See A., 1942, I, 306.

Calculation of steric hindrance.—See A., 1942, I, 259.

Nitration of methane.—See B., 1942, II, 209.

Preparation of nitrohydroxy-compounds of the paraffin series.—See B., 1942, II, 212.

Organic acid synthesis.—See B., 1942, II, 213.

Preparation of organic acids from olefines and carbon monoxide.—See B., 1942, II, 213.

Mixed electrolyses of nitrate with *n*-valerates and *iso*butylacetates. M. Rudin (*Helv. Chim. Acta*, 1942, **25**, 636—640).—The products of the mixed electrolysis of nitrate and *n*-valerate are *n*-octane, $Bu^{\alpha}OH$ characterised as $Bu^{\alpha}O{\cdot}NO$, $Bu^{\alpha}NO_3$, and $Bu^{\alpha}CO_2Bu^{\alpha}$, $(CHMe{:})_2$, leading to butane-$\beta\gamma$-diol dinitrate, and an octanediol dinitrate. *iso*Butylacetic acid [γ-methyl-*n*-valeric acid] similarly affords $\beta\eta$-dimethyloctane, (?) *iso*amyl nitrite, and nitrates or *iso*butylacetates of a decanol, b.p. 106—108°/22 mm., or decanediol, b.p. 133—140°/14 mm. H. W.

Formation of carbonyl compounds by the enzymic oxidation of unsaturated fatty acids. H. Süllmann (*Helv. Chim. Acta*, 1942, **25**, 521—523).—CO-compounds, capable of forming hydrazone, dihydrazone, and osazone derivatives, are formed during the oxidation of linolenic acid by lipoxidase. H. W.

Dihydroxystearic acid of castor oil; its constitution and structural relationship to the $\theta\iota$-dihydroxystearic acids, m.p. 132° and 95°, respectively. G. King (*J.C.S.*, 1942, 387—393; cf. A., 1939, II, 5).—Dry HCl is passed through the naturally occurring dihydroxystearic acid (**I**), m.p. 141°, of castor oil at 160°, to give mixed chlorohydroxystearic acids, converted by boiling 2N-NaOH– or -KOH–EtOH into (d-)*oxidostearic acid* (**II**), m.p. 59·5°, $[\alpha]_D^{19}$ +0·29° in EtOH, hydrolysed by 7N-KOH at 170° (sealed tube) to *r*-dihydroxystearic acid (**III**), m.p. 95°. (**I**) and conc. HCl at 160° afford chlorohydrins and thence (**II**), with (probably) θ- and ι-ketostearic acid. *r*-Dihydroxystearic acid (**IV**), m.p. 332°, and dry HCl at 160° give chlorohydrins and thence *r*-oxidostearic acid, m.p. 59·5° [not identical with (**II**), but identical with the acid obtained from oleic acid by HOCl, followed by NaOEt–EtOH], and (**III**). (**III**) by the above procedure yields *r*-oxidostearic acid, m.p. 55·5° (identical with that obtained by autoxidation of elaidic acid), and thence (**IV**). The optical inversion involved in these transformations probably occurs during hydration of the oxide ring, and it is concluded that (**I**) is an active component of (**IV**). Configurations are assigned to the acids. A. T. P.

Autoxidation of "oxygen-active" acids. I. Gravimetric and volumetric course of the addition of oxygen to the methyl esters. W. Treibs (*Ber.*, 1942, **75**, [*B*], 203—210).—In uncatalysed action Me eleostearate rapidly absorbs 2 atoms of O; further absorption takes place very slowly and ceases before complete reaction with 3 O. In contrast to the other acids there is no elimination of H_2O in the absence of a catalyst but such is induced by impurities in the air and filter-paper used as a support for the ester. Me linoleate absorbs 4 O and loses 1 H_2O; further action of O_2 causes the production of large fragments. Me linolenate consumes 5 O and loses 2 or 1 H_2O according to conditions. Syneresis does not lead to formation of large fragments. The hexaenic ester of liver oils reacts with 7 O and eliminates 1 H_2O; further oxidation is not observed. H. W.

Oxalic acid from sawdust.—See B., 1942, II, 209.

Formation of complexes of tartaric and metatungstic acids.—See A., 1942, I, 305.

β-Methylallyl-substituted malonic ester.—See B., 1942, II, 214.

Manufacture of succinic anhydride.—See B., 1942, II, 214.

Alkylsuccinic acids. I. *n*-Tetradecyl- and *n*-hexadecyl-succinic acids. S. U. Mehta and K. S. Nargund (*J. Univ. Bombay*, 1942, **10**, *Part* 5, 141—142).—n-*Hexadecane-aaβ-tricarboxylic acid*, m.p. 135°, on pyrolysis gives *n*-tetradecylsuccinic acid, m.p. 110° (lit. 121°) (*Me*$_2$, b.p. 220°/20 mm., and *Et*$_2$ ester, b.p. 230°/20 mm.; anhydride, m.p. 74°; *imide*, m.p. 98—99°; *monoanilide*, m.p. 124—125°; *mono-p-toluidide*, m.p. 118—120°). n-*Octadecane-aaβ-tricarboxylic acid*, m.p. 135°, on pyrolysis gives n-*hexadecylsuccinic acid*, m.p. 89—90°, (*Me*$_2$, b.p. 205—210°/10 mm., and *Et*$_2$ ester, b.p. 215—220°/10 mm.; *anhydride*, m.p. 63°; *imide*, 94—95°). W. C. J. R.

Purification of maleic anhydride.—See B., 1942, II, 214.

Effect of inorganic salts on ketone decomposition of oxaloacetic acid.—See A., 1942, I, 302.

Synthesis of aminopropanols. I. O. Hromatka (*Ber.*, 1942, **75**, [*B*], 131—138).—1-γ-Hydroxypropylpiperidine, b.p. 223°/750 mm. (hydrochloride, m.p. 151°; picrate, m.p. 69°; methiodide, m.p. 133—134°; benzoate hydrochloride, m.p. 190—191°; *p*-nitrobenzoate hydrochloride, m.p. 211°), is prepared by heating piperidine (**I**) with $CH_2{:}CH{\cdot}CH_2{\cdot}OH$ and $CH_2{:}CH{\cdot}CH_2{\cdot}ONa$ (**II**) at 100°, or by reduction of Et β-piperidinopropionate, b.p. 123°/20 mm. [from (**I**) and $CH_2{:}CH{\cdot}CO_2Et$], by Na–EtOH or by H_2 at 203°/234 atm. in presence of a $CuO{-}Cr_2O_3$ catalyst. (**II**) and morpholine at 108° slowly give 4-γ-hydroxypropylmorpholine, b.p. 143—145°/28 mm. (*picrate*, m.p. 136—137°; *aurichloride*, m.p. 125—127°; *benzoate hydrochloride*, m.p. 190°; p-*nitrobenzoate hydrochloride*, m.p. 238°). $NHEt_2$ and (**II**) at 110—120° give $NEt_2{\cdot}[CH_2]_3{\cdot}OH$, b.p. 122°/70 mm., in 46·7% yield. Under similar conditions $NHMeBu^{\beta}$ affords $NMeBu^{\beta}{\cdot}[CH_2]_3{\cdot}OH$ (**III**) (*benzoate picrate*, m.p. 96—98°; p-*nitrobenzoate hydrochloride*, m.p. 152—154°). (**III**) is also obtained by the reduction (Na–EtOH at 130°) of *Et β-methyl*sec.*-butylaminopropionate*, b.p. 102—105°/13 Torr. $CHMeBu^{\beta}{\cdot}NHMe$ gives γ-*methyl-β'-iso*hexylaminopropan-a-*ol*, b.p. 115—120°/13 Torr (p-*nitrobenzoate hydrochloride*, m.p. 127—128°). NHPhMe and (**II**) at 108° afford *methyl-γ-hydroxypropylaniline*, b.p. 180—185°/25 Torr. $NHPr^{\beta}_2$ and $NHBu^{\beta}_2$ could not be caused to react with $CH_2{:}CH{\cdot}CO_2Et$. H. W.

Formation of glycine from serine. F. Leuthardt and B. Glasson (*Helv. Chim. Acta*, 1942, **25**, 245—249).—Hippuric acid is formed from serine and BzOH but the yield of glycine obtained on hydrolysis is < that obtained with glutamine under similar conditions. H. W.

Structural specificity of choline and betaine in trans-methylation.—See A., 1942, III, 619.

Stereoisomeric aa′-iminodipropionic acids. P. Karrer and R. Appenzeller (*Helv. Chim. Acta*, 1942, **25**, 595—599).—*l*(+)-*aa′-Iminodipropionic acid*, m.p. 247° (corr.; decomp.), $[\alpha]_D^{14}$ +12·1° in H_2O, is obtained by condensation of *d*(+)-$CHMeBr{\cdot}CO_2H$ with *l*(+)-$NH_2{\cdot}CHMe{\cdot}CO_2H$ in presence of NaOH; the l-*acid*, m.p. 247° (corr.; decomp.), $[\alpha]_D^{15}$ −11·0° in H_2O, is obtained analogously from the (−)-acids. meso-*aa′-Iminodipropionic acid*, m.p. ~232—233° (decomp.), is derived by use of a (−)- with a (+)-reactant, the Walden inversion being complete. H. W.

***β-dl-$\alpha'\beta'$*-Dihydroxy-*β'*-methylbutyramidopropionic acid.** W. Schindler and T. Reichstein (*Helv. Chim. Acta*, 1942, **25**, 551—554).—$CMe_2{:}CH{\cdot}CO_2H$ is oxidised by OsO_4 and $AgClO_3$ and then esterified (CH_2N_2) to *Me aβ-dihydroxy-β-methylbutyrate*, b.p. 58—60°/0·2 mm. (corresponding amide and hydrazide are non-cryst.). $CMe_2{:}CH{\cdot}COCl$ and $NH_2{\cdot}[CH_2]_2{\cdot}CO_2Et$ give *Et β-dimethylacrylamidopropionate*, b.p. 115—117°/0·08 mm.; hydrolysed to the *acid*, m.p. 100—101°. This is oxidised by OsO_4 and $AgClO_3$ and then esterified to *Me* β-dl-$\alpha'\beta'$-*dihydroxy-β′-methylbutyramidopropionate*, b.p. 105—108° (bath)/

0·005 mm. (*benzylthiuronium* salt of the corresponding acid, m.p. 154—156°). H. W.

Ureides containing a quaternary carbon atom.—See B., 1942, II, 216.

Pyrolysis of methyl and ethyl cyanides. B. S. Rabinovitch and C. A. Winkler (*Canad. J. Res.*, 1942, **20**, **B**, 69—72).—HCN is a primary product of the thermal decomp. of MeCN at 865° and 675°. Final products are H_2, CH_4, HCN, C, small quantities of C_2 hydrocarbons, and products of high b.p. The products of the thermal decomp. of EtCN are H_2, CH_4, C_2H_6, C_2H_4, HCN, MeCN, acrylonitrile, C, small amounts of succinonitrile, and compounds of higher b.p. A. J. M.

II.—SUGARS AND GLUCOSIDES.

Supersensitive Schiff's aldehyde reagent. Demonstration of a free aldehyde group in certain aldoses. W. C. Tobie (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 405—406).—The reagent is a 0·05% solution of basic fuchsin in 0·1% aq. SO_2. With aldose sugars a pink colour is formed. J. D. R.

So-called *iso*sucrose. H. H. Schlubach and B. Middelhoff (*Annalen*, 1942, **550**, 134—140).—The action towards enzymes of *iso*sucrose obtained by Irvine *et al.* (A., 1929, 683) from the octa-acetate, m.p. 133·5°, and NaOMe supports the view that it is an isomeride of turanose; it is regarded as *iso*turanose. A. T. P.

Preparation of aldehydo-acylated ribose.—See B., 1942, II, 216.

Heart glucosides. XIX. Lactone ring of scilliroside. A. Stoll and J. Renz (*Helv. Chim. Acta*, 1942, **25**, 377—391).—The doubly unsaturated, 6-membered lactone ring of scilliroside (**I**) is characterised by the presence of OAc in the α-position to CO. The possibility of " isomerisation " proves that (**I**), like scillarene *A* (**II**) has a *tert.*-OH at $C_{(14)}$. The action of KOH–MeOH on (**I**) is in essence similar to that on (**II**) but the product does not form stable, homogeneous alkali enolates. With $Ba(OMe)_2$ (**I**) slowly yields a cryst. non-homogeneous ppt. which after acidification reacts to only a slight extent with CH_2N_2; the substance appears to react mainly in the carbonyl form but homogeneous products could not be isolated. (**I**) and KOH–MeOH yield *Me deacetylscillirosidate* (**III**), converted by *o*-$C_6H_4(NH_2)_2$ into a *quinoxaline* derivative, $C_{37}H_{50}O_{10}N_2$. The corresponding acid loses CO_2 when treated with H_2O_2 but a homogeneous oxidation product could not be obtained. The reactions, however, decide the location of Ac in (**I**). With Ac_2O (**III**) gives an amorphous *hexa-acetate*, m.p. (indef.) 130—140°. (**III**) loses H_2O in EtOH–AcOH and becomes isomerised to the amorphous *Me deacetylisoscillirosidate* (**IV**), decomp. ~210°, which does not react with CH_2N_2 and gives an amorphous *dinitrophenylhydrazone*, decomp. 160—170°. (**IV**) is converted by Ac_2O–C_5H_5N into the cryst. *penta-acetate* (**V**), m.p. 242°, $[\alpha]_D^{20}$ −46° in MeOH. The *penta-acetate* of the corresponding Et ester has m.p. 228°, $[\alpha]_D^{20}$ −44° in MeOH. Hydrogenation (PtO_2 in MeOH) of (**V**) gives a *substance*, $C_{39}H_{56}O_{14}$, m.p. 138°, $[\alpha]_D^{20}$ −5·6° in MeOH, deacetylated by $Ba(OMe)_2$ in MeOH at 0° to the *compound*, $C_{31}H_{48}O_{10}$, $[\alpha]_D^{20}$ −25° in MeOH, and deacetylated and demethylated by NaOH–MeOH to the *substance*, $C_{30}H_{46}O_{10}$, m.p. 210°, $[\alpha]_D^{20}$ −26° in MeOH. M.p. are corr. H. W.

Carboxyl content of fibre- and wood-cellulose. E. Husemann and O. H. Weber (*J. pr. Chem.*, 1942, [ii], **159**, 334—342).—Determination of the CO_2H content of purified celluloses (**I**) by the " reversible methylene-blue method " shows that wood-(**I**) contain 1 CO_2H for 103—109 glucose residues whereas fibre-(**I**) have very high glucose vals. The high CO_2H content of cotton after purification with ClO_2 and NaOH is caused by slight impurity (pectins). Comparison of the glucose vals. with the viscosimetrically determined mean degrees of polymerisation shows the fibre-(**I**) to be approx. monocarboxylic acids, thus indicating that CO_2H is formed by oxidation of the terminal reduced glucose residues. Wood-(**I**) are polycarboxylic acids in which a macromol. contains 9—12 CO_2H and thus resemble the xylans which with the degree of polymerisation 150 have a xylose val. 16. The function of CO_2H in the plant cell is discussed. H. W.

Cuprietylenediamine as a solvent for cellulose fractionation. F. L. Straus and R. M. Levy (*Paper Trade J.*, 1942, **114**, *TAPPI Sect.*, 211—215; cf. B., 1942, II, 224).—A method is described for the fractional pptn. of cellulose (flax and cotton) (**I**), from its solution in 0·5M-$Cu(OH)_2$–$(CH_2{\cdot}NH_2)_2$ (**II**) by means of 8N-H_2SO_4 at 25°, each fraction being centrifuged, washed, dried, redissolved in (**II**), and its η measured. The amount of (**I**) in each fraction is then determined in an aliquot portion by complete pptn. with H_2SO_4 followed by oxidation with $K_2Cr_2O_7$. The nature of the (**I**)–(**II**) complex is discussed mathematically in relation to the results obtained. H. A. H.

III.—HOMOCYCLIC.

Kinetics of the formation and decomposition of di*cyclo*pentadiene. E. Baur and S. Fratter (*Helv. Chim. Acta*, 1941, **24**, 768—782).—Manometric determinations of the formation and dissociation of di*cyclo*pentadiene at 149°, 165·5°, 180°, and 195° and 109—638 mm. disclose systematic departures from the requirements of Guldberg's kinetic postulate. In the sense of Baur's kinetics, these discrepancies indicate onesidedness of the production of equilibrium. H. W.

Light absorption of geometrical isomerides and structure of vitamin-*D*. H. P. Koch (*Chem. and Ind.*, 1942, 273—275).—For *cis–trans*-isomerides or pairs of substances containing geometrically isomeric chromophores, the *cis*-form shows a much smaller extinction coeff. (ε). Steric hindrance is considered to be responsible for the feeble light absorption properties of various 2-methyl-Δ^1-*cyclo*hexene derivatives. The abnormally low ε for vitamin-*D* (calciferol) supports the postulated structure; the factors preventing free rotation to form the stable *trans*-configuration are unknown. H. B.

Raman spectra of monoalkylbenzenes and monoalkyl*cyclo*hexanes.—See A., 1942, I, 258.

Bromination of *o*-nitrotoluene. Steric effect of bromine on the relative yields of the 4- and 6-bromo-derivatives. D. R. Mehta and P. Ramaswami Ayyar (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 99—109).—Thermal analysis of the reaction products of the bromination of *o*-$C_6H_4Me{\cdot}NO_2$ (**I**) in the presence of C_5H_5N, $Fe_2(SO_4)_3$–H_2SO_4, Fe, Fe–I (the most effective catalyst), Sb, $SbCl_3$, and $SbCl_5$ shows an average yield of 57% of 1 : 4 : 2- and 43% of 1 : 6 : 2-$C_6H_3MeBr{\cdot}NO_2$. (**I**) with Cl_2 affords 66% of 1 : 6 : 2-$C_6H_3MeCl{\cdot}NO_2$; the lower yield with Br may be due to its larger at. vol. W. C. J. R.

Sesquiterpenes. LIII. Synthesis of 5-methylazulene. P. A. Plattner and H. Roniger (*Helv. Chim. Acta*, 1942, **25**, 590—594).—5-Chloromethylindane is dehalogenated (H_2–Pd–C in EtOH) to *5-methylindane*, b.p. 74°/11 mm., converted by treatment with $CHN_2{\cdot}CO_2Et$ at 130—140° and then at 165°, followed by hydrolysis and distillation over Pd–C, into *5-methylazulene* [*picrate*, m.p. 110·5°; additive *compound*, m.p. 151·5°, with 1 : 3 : 5-$C_6H_3(NO_2)_3$]. M.p. are corr. H. W.

Preparation of β-amino-α-phenylpropane.—See B., 1942, II, 273.

Antiplasmodial action and chemical constitution. V.—See A., 1942, II, 288.

Molecular compounds of carbamide derivatives. E. Ochiai and S. Kuroyanagi (*J. pr. Chem.*, 1941, [ii], **159**, 1—12; cf. A., 1939, II, 363).—F.p. diagrams show that compound formation does not occur between $NH_2{\cdot}CO{\cdot}NH{\cdot}COEt$ (**I**), m.p. 204° (lit. 210—211°), and *p*-$NO_2{\cdot}C_6H_4{\cdot}OH$ (**II**) or 2-thiol-4-methylthiazole (**III**). $CO(NH{\cdot}COEt)_2$ (**IV**), however, gives 1 : 1 mol. *compounds* with (**II**), (**III**), $NH_2{\cdot}CO{\cdot}NHPh$ (**V**), and $NH_2{\cdot}CS{\cdot}NHPh$ (**VI**), and 2 : 1 *compounds* with *m*-$C_6H_4(OH)_2$ (**VII**) and $NHPh_2$. Compounds are not formed from (**IV**) and pyramidone, veronal, *m*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, or sulphathiazole, from (**VI**) and (**II**), (**VII**), or (**V**), from $NH_2{\cdot}CS{\cdot}NH{\cdot}CH_2Ph$, $NH_2{\cdot}CS{\cdot}NHAc$, or Et 2-thiol-4-methylglyoxaline-5-carboxylate with (**II**) and (**VII**). (**III**) yields *compounds* with (**VII**) (3 : 1) and (**II**) (1 : 1). Although $CO(NH_2)_2$ does not give a compound with (**I**) or (**V**), it forms a 1 : 1 *compound* with (**IV**). A. T. P.

Carbimides. Reaction between phenylcarbimide and sodium phenylacetylide. A. Tyabji (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 110—113).—PhNCO and CNa:CPh in Et_2O (2 days) afford a *compound*, $C_{29}H_{21}O_3N_3$, m.p. 260°, and *isomerides*, $C_{22}H_{16}O_2N_2$, m.p. 201° (**I**) and 186° (**II**). (**I**) yields a Br_1-derivative, m.p. 190—191°. Attempted prep. of the phenylcarbamate of 4-hydroxy-2-phenylquinoline for comparison with (**I**) or (**II**) was unsuccessful. W. C. J. R.

Theory of the benzidine rearrangement. A. Pongratz and K. Scholtis (*Ber.*, 1942, **75**, [*B*], 138—145).—$(NPhAc)_2$ is not attacked by cold MeI or conc. acids, thus showing that formation of benzidine (**I**) from $(NHPh)_2$ (**II**), is an ionic change when effected by conc. acids; this view is supported by the existence of salts of (**II**) with conc. acids and their established isomerisation in aq. and non-aq. media. The change occurs with the cation since the isomerisation of unsymmetrical hydrazobenzenes invariably yields exclusively the corresponding unsymmetrical (**I**) form and not mixed forms as would be expected from an extra-mol. course of the change. The suggested scheme is: (**II**) $+2HX \rightarrow [(NH_2Ph)_2]X_2 \rightarrow [C_6H_4{\cdot}NH_2]_2X_2$. The transformation by MeI is regarded as a cryptoionic change. The driving force of the isomerisation is the considerable difference in energy content of the two systems. NPhAc·NHPh and MeI at 100° yield N-*acetyl*-N′N′-*dimethylbenzidine methiodide di-iodide*, m.p. 205—206°, converted by Na_2SO_3 into N-*acetyl*-N′N′-*dimethylbenzidine methiodide*, m.p. 228° after softening. $(NPhAc)_2$ and MeI do not react at 100° but in presence of MeOH a primary hydrolysis occurs with ultimate resulting formation of $[C_6H_4{\cdot}NMe_3I]_2I_4$ (**III**). (**II**) and cold MeI in a closed vessel shielded from light rapidly give *hydrazobenzene dihydriodide*; this is also obtained from the reactants at 100° but is then accompanied by (**III**) if the reaction is prolonged. $(NPhMe)_2$ and MeI give *dimethylhydrazobenzene dimethiodide*. (**II**) and MeI under N_2 at 100° yield benzidine dihydriodide, m.p. >270°, which with MeI and MeOH at 100° gives (**III**) and tetra-

methylbenzidine dimethiodide whereas the last-named is formed almost exclusively from (I) under like conditions. Prolonged heating of $(C_6H_4{\cdot}NMe_2)_2$,2HI with MeI and MeOH at 100° in an air-free tube leads to (III). (II) and MeBr in a sealed tube at room temp. slowly yield *hydrazobenzene dihydrobromide*. H. W.

Course of the coupling of dialkylated anilines. K. Holzach and A. Simon (*Ber.*, 1942, **75**, [*B*], 166—167).—4-*Nitro*-, m.p. 122°, 2-*chloro*-4-*nitro*-, m.p. 85·5°, 2 : 4-*dinitro*-, m.p. 110° and 6-*bromo*-2 : 4-*dinitro*-, m.p. 122°, -4′-*di*-n-*butylazobenzene* are obtained by coupling the requisite diazonium salt with $NPhBu^{\alpha}_2$. There is no evidence of the elimination of an alkyl group or production of a monoalkyl dye. The presence of strongly negative substituents does not inhibit normal coupling. H. W.

Solubilisation of diazoimino-compounds.—See B., 1942, II, 279.

Mixed triaryl thiophosphates.—See B., 1942, II, 279.

Aquo-ammono-phosphoric acids. II. Preparation of *N*-substituted derivatives of the phenyl esters of amido- and diamido-phosphorio acids. L. F. Audrieth and A. D. F. Toy (*J. Amer. Chem. Soc.*, 1942, **64**, 1337—1339).—*N*-Substituted derivatives of (*a*) Ph_2 amido- and (*b*) Ph diamido-phosphates can be prepared by aminolysis either of the corresponding chlorophosphates or of the $POCl_3$–PhOH–C_5H_5N reaction mixture. The latter method is satisfactory for (*b*), but is not recommended for (*a*). *Ph di*(*methylamido*)-, m.p. 103—105°, *di*(cyclo*hexylamido*)-, m.p. 124—125°, and *di*(*morpholido*)-*phosphate*, m.p. 85—86°, and *Ph*$_2$ *methylamido*-, m.p. 95°, cyclo*hexylamido*-, m.p. 104—105°, and *morpholido-phosphate*, m.p. 72·5—73·5°, are new. W. R. A.

Cleavage of ethers by boron bromide. I. Common ethers. F. L. Benton and T. E. Dillon (*J. Amer. Chem. Soc.*, 1942, **64**, 1128—1129).—R_2O (R = Et, Pr$^{\beta}$, or Bu$^{\alpha}$) (3 mols.) and BBr_3 (1 mol.) give good yields of ROH + RBr. PhOPr$^{\beta}$, PhOBu$^{\alpha}$, *o*-$C_6H_4Br{\cdot}OMe$, and 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}OMe$ give good yields of phenol and alkyl halide. $CH_2Ph{\cdot}OPr^{\alpha}$ gives $Pr^{\alpha}OH$ (71%) and CH_2PhBr (75%). R. S. C.

Synthesis of allyl and propenyl essential oils. General method. L. Bert (*Compt. rend.*, 1941, **213**, 873—874).— $OR{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{:}CHCl$ (from PhOR, $CH_2Cl{\cdot}CH{:}CHCl$, and $AlCl_3$ or Zn dust) afford (with other products) (i) $OR{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{:}CH_2$ by Na (alone or in Et_2O or a C_6H_6 hydrocarbon), (ii) $OR{\cdot}C_6H_4{\cdot}CH{:}CHMe$ by treatment with KOH–R′OH (whence $OR{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OR'$) then Na + EtOH. Estragol, safrole, methyleugenol, elemicin, anethole, *iso*safrole, *iso*-methyleugenol, *iso*elemicin, and asarone have been thus obtained. W. C J. R.

Reduction of aromatic nitro- and polynitro-compounds. XV. Cathodic reduction of nitrophenol ethers. K. Brand and W. Schreber [with, in part, E. Heck] (*Ber.*, 1942, **75**, [*B*], 156—165; cf. A., 1935, 482).—The cathodic reduction of *o*-nitrophenyl acetate or benzoate is rendered impossible by the ease with which the esters are hydrolysed, but satisfactory results are obtained with o- (**I**), b.p. 154°/16 mm., f.p. 30·5°, and p- (**II**), b.p. 166°/14 mm., f.p. 21·2° *-nitrophenyl OMe·CH*$_2$ *ether*, obtained from $CH_2Cl{\cdot}OMe$ and the dry Na or Li salt of the NO_2-phenol. Reduction of (**I**) at a Hg cathode [anolyte is aq. Na_2CO_3 free from NaCl; catholyte is a solution of (**I**) in EtOH–H_2O–NaOAc] gives a mixture of the expected azoxy- (**III**) and hydrazo- (**IV**) -ethers, which are not isolated. (**III**) is converted by HCl into 2 : 2′-azoxyphenol, m.p. 153°. (**IV**) is oxidised by air to 2 : 2′-*dimethoxymethoxyazobenzene*, m.p. 103·5° hydrolysed by HCl to 2 : 2′-azophenol, m.p. 174° (whence 2 : 2′-azoanisole, m.p. 154·5°, and 2-hydroxy-2′-methoxyazobenzene, m.p. 122°). Under these conditions the yields of (**III**) and (**IV**) are small, but if a Ni is substituted for a Hg cathode the yield of (**IV**) is increased to 40—60% and (**III**) is obtained in small quantity. At a Ni cathode (**II**) gives a 69—70% yield of 4 : 4′-*dimethoxymethoxyazobenzene*, m.p. 82—83°, not apparently accompanied by the azoxy-ether. It is hydrolysed to 4 : 4′-azophenol, m.p. 211°. With MeOH–NaOMe (**I**) and (**II**) exchange $OMe{\cdot}CH_2$ for Me before reduction to the azoxyanisole occurs. p-*NO*$_2{\cdot}C_6H_4{\cdot}OLi$ (+3H_2O) is described. H. W.

Thermal rearrangement of *m*-acetamidophenyl allyl ether. R. T. Arnold, J. McCool, and E. Schultz (*J. Amer. Chem. Soc.*, 1942, **64**, 1023—1025).—*m*-$NHAc{\cdot}C_6H_4{\cdot}OH$, $CH_2{:}CH{\cdot}CH_2Br$, and K_2CO_3 in $COMe_2$ give m-*acetamidophenyl allyl ether*, m.p. 87—88°, rearranged in boiling $NPhMe_2$–H_2 or –N_2 (not in ligroin, b.p. 200—220°) into 5-*acetamido*-2-*allylphenol*, m.p. 160·5—162° [*acetate* (**I**), m.p. 132—133°]. H_2–PtO_2 and (**I**) in EtOH give (after hydrolysis with aq. K_2CO_3) 5-*acetamido*-2-*propylphenol* (**II**), m.p. 173·5—174°, hydrolysed by HCl to 5 : 2 : 1-$NH_2{\cdot}C_6H_3Pr^{\alpha}{\cdot}OH$, m.p. 132—132·5° [with Ac_2O gives the *acetate*, m.p. 117·5—118°, of (**II**), converted thereinto by aq. Na_2CO_3 + NaOH], which is also obtained by the method of Hartung *et al.* (A., 1941, II, 131), who obtained a form, m.p. 109—110°. 3 : 4 : 1-$NO_2{\cdot}C_6H_3Pr^{\alpha}{\cdot}NH_2$ [prep. from 1 : 2 : 4-$C_6H_3Pr^{\alpha}(NO_2)_2$ by H_2S–NH_3–H_2O–EtOH], m.p. 59—59·5°, gives (diazo-reaction) 3-*nitro*-, m.p. 46·5—47·5°, reduced by H_2–Pt in EtOH to 3-*amino*-4-n-*propylphenol*, m.p. 152—153° (acetylation gives oils). R. S. C.

Action of thionyl chloride on β-naphthol and 1-hydroxy-2-naphthoic acid. J. W. Airan and S. V. Shah (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 128—130).—β-$C_{10}H_7{\cdot}OH$, $SOCl_2$, and $BiCl_3$ in Et_2O or C_6H_6 afford 2 : 2′-dihydroxy-1 : 1′-dinaphthyl sulphide, m.p. 212°, whilst 1 : 2-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$ similarly yields 4 : 4′-dihydroxy-3 : 3′-dicarboxy-1 : 1′-dinaphthyl sulphide, m.p. 265°. W. C. J. R.

Interaction of sulphuryl chloride and naphthol derivatives. J. W. Airan and S. V. Shah (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 131—134).—α-$C_{10}H_7{\cdot}OH$, SO_2Cl_2, and $BiCl_3$ in Et_2O afford 4 : 1-$C_{10}H_6Cl{\cdot}OH$; 2 : 1-$C_{10}H_6Ac{\cdot}OH$ similarly gives 4-*chloro*-2-*acetyl*-1-*naphthol*, m.p. 116° (*acetate*, m.p. 82°); 1 : 2-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$ yields 1 : 4 : 2-$OH{\cdot}C_{10}H_5Cl{\cdot}CO_2H$ (*acetate*, m.p. 102°); 2 : 3-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$ gives 3 : 4 : 2-$OH{\cdot}C_{10}H_5Cl{\cdot}CO_2H$ (*acetate*, m.p. 186°). W. C. J. R.

Preparation of alkali formaldehydesulphoxylate–diaminodiphenyl sulphide or sulphone reaction products.—See B., 1942, II, 279.

Dielectric polarisation of benzyl alcohol.—See A., 1942, I, 293.

Synthesis of "heavy" *dl*-adrenaline. G. R. Clemo and G. A. Swan (*J.C.S.*, 1942, 395—397).—All six H of *o*-$C_6H_4(OH)_2$ exchange with D_2O in alkaline solution at 100°, although replacement of the last is very slow. The "*heavy*" *pyrocatechol*, m.p. 104°, used for subsequent reactions, was approx. $C_6HD_5O_2$. With $CD_2Cl{\cdot}CO_2D$ and $POCl_3$ at 55—60°, followed by hot D_2O, it affords "heavy" chloroacetylpyrocatechol, m.p. 172° (85·5 atoms % D), converted by $CD_3{\cdot}ND_2$ in D_2O at room temp. into "heavy" adrenalone, and thence by hot dil. D_2O–D_2SO_4 into the "heavy" sulphate, which is reduced (D_2, Pd-C, D_2O) to "heavy" *dl*-adrenaline (90 atoms % D, *i.e.* $C_9H_{11\cdot3}D_{11\cdot7}O_3N$). Its physiological action is almost indistinguishable from that of "light" *dl*-adrenaline. A. T. P.

Substituted cinnamic acid esters and amides.—See B., 1942, **II**, 280.

Attempted direct synthesis of β-substituted cinnamic acids. B. D. Patel and K. V. Bokil (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 123—127).—Condensation of $CH_2Ac{\cdot}CO_2Et$ (**I**) with phenolic ethers in presence of varying [H_2SO_4] is studied; concns. <80% are ineffective. 80% H_2SO_4 yields substituted butyric acids and/or esters and more complex acids (**II**) formed by addition of (**I**) to any cinnamic acid (**III**) or ester formed. 85% H_2SO_4 gives (**II**) and sulphonated acids. Contrary to Limaye (A., 1940, II, 129) no substituted (**III**) has been obtained. PhOEt and (**I**) yield *ββ-di*-p-*phenetylbutyric acid*, m.p. 60—62° (anilide, m.p. 135°), also obtained from *p*-$OEt{\cdot}C_6H_4{\cdot}CMe{:}CH{\cdot}CO_2H$ and PhOEt in 80% H_2SO_4. *o*-$C_6H_4Me{\cdot}OMe$ and (**I**) yield *ββ-di*-6-*methoxy*-m-*tolylbutyric acid*, m.p. 131—132° (anilide, m.p. 141—142°); *m*-$C_6H_4Me{\cdot}OMe$ yields 4 : 7-dimethylcoumarin, m.p. 132—133°; *p*-$C_6H_4Me{\cdot}OMe$ gives 4 : 6-dimethylcoumarin, m.p. 150—151°. W. C. J. R.

Synthesis of 3′ : 5′-di-iodothyronine. P. Block, jun., and G. Powell (*J. Amer. Chem. Soc.*, 1942, **64**, 1070—1074).—Iodination of thyronine gives mixtures (cf. lit.). *K* 2 : 6-*di-iodo*-4-*nitrophenoxide* best (~80%) prepared from *p*-$NO_2{\cdot}C_6H_4{\cdot}OH$ by ICl–AcOH–H_2O etc. at 95°, with Me_2SO_4–K_2CO_3–$PhNO_2$ at 130° gives the Me ether (85%), reduced by Fe–AcOH to 4 : 2 : 6 : 1-$NH_2{\cdot}C_6H_2I_2{\cdot}OMe$ (90%), m.p. 105° (lit. 100°). A diazo-reaction ($OBu{\cdot}NO$–H_2SO_4–AcOH at 15—18°; then H_2SO_4–H_2O at 110°) then yields 2 : 6-*di-iodoquinol* 1-*Me ether* (75%), m.p. 125—125·5° (derived *Me*$_2$ *ether*, m.p. 56°, also obtained from 4 : 3 : 5 : 1-$NO_2{\cdot}C_6H_2I_2{\cdot}OH$ by way of the quinone), which with *p*-$C_6H_4Cl{\cdot}NO_2$–KOH–H_2O (little) at 130° (later 160°) gives 3′ : 5′-*di-iodo*-4-*nitro*-4′-*methoxydiphenyl ether* (70%), m.p. 124—124·5°, reduced by H_2–$Pd(OH)_2$–$CaCO_3$ in EtOH–NaOH (little) to *p*-$NH_2{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4{\cdot}OMe$-*p* (**I**) and by Fe filings + powder in EtOH–H_2O–AcOH at 100° to 3′ : 5′-*di-iodo*-4-*amino*-4′-*methoxydiphenyl ether* (90%), m.p. 105·5° [hydrochloride, m.p. 232—233°; Ac derivative, m.p. 176·5°, hydrogenated as above to (**I**)]. By the Sandmeyer reaction this yields p-3′ : 5′-*di-iodo*-4′-*methoxyphenoxybenzonitrile* (40%), softens at 133·5—134·5°, m.p. 138·5—139·5°, reduced (Stephen) to the *aldehyde* (55%), m.p. 119° after softening, which by way of the azlactone gives *α-benzamido*-p-3′ : 5′-*di-iodo*-4′-*methoxyphenoxycinnamic acid* (85%), m.p. 230—231°. With red P–HI–AcOH–H_3PO_2 and then HBr this gives, first, 3′ : 5′-*di-iodothyronine Me ether*, decomp. 212° (preheated at 190°), and then mainly 3′ : 5′-*di-iodothyronine*, decomp. 206° (preheated at 190°) [reduced by H_2–$Pd(OH)_2$–$CaCO_3$ in aq. NaOH to thyronine], which is <¼ as active (? inactive) as thyroxine. R. S. C.

Syntheses in the chaulmoogric acid series. IV. Synthesis of *β-dl*-Δ^2-*cyclo*pentenylpropionic acid, a new homologue of chaulmoogric acid. K. V. Bokil and K. S. Nargund (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 118—122).—Reduction (Na–Hg, 80% EtOH) of Et *cyclo*pentanone-2-carboxylate-5-β-propionate (cf. Cook *et al.*, A., 1934, 1002) and dehydration (Ac_2O) of the OH-acid yields a mixture separated by fractionation of the Ba salts from EtOH. The less sol. salt gives an unsaturated dibasic *acid*, $C_9H_{12}O_4$, m.p. 128—129°. The sol. salt gives mixed Et esters whence the Et ester, b.p. 90—92°/7 mm., of β-Δ^2-cyclo*pentenylpropionic acid*, b.p. 127—129°/7 mm. Et Δ^1- or Δ^2-*cyclo*pentene-1-carboxylate is reduced (Na, EtOH) to Δ^1-cyclo*pentenylcarbinol*, b.p. 57/10 mm. (p-*nitrobenzoate*, m.p. 36—37°). W. C. J. R.

Synthesis of anti-leprosy drugs. I. New synthesis of *κ-cyclo*hexylundecoic acid, an analogue of dihydrohydnocarpic acid. (Miss)

B. C. Pandya, K. S. Nargund, and K. V. Bokil (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 114—117).—Et potassio*cyclo*hexanone-2-carboxylate (modified prep.) and Et κ-bromoundecoate in C_6H_6 afford *Et* cyclo*hexanone-2-carboxylate-2-κ-undecoate*, b.p. 260—265°/13 mm., hydrolysed by boiling conc. HCl to 2-*carbethoxy*cyclo*hexanone-2-κ-undecoic acid*, b.p. 260—265°/3 mm., and by KOH–MeOH to the crude dibasic acid, which on distillation gives κ-2-*keto*-cyclo*hexylundecoic acid*, m.p. 61—62° (Et ester, b.p. 210—215°/3 mm.; semicarbazone, m.p. 134—135°), reduced (Clemmensen) to κ-*cyclo*hexylundecoic acid, m.p. 57—58° (Et ester, b.p. 193—195°/3 mm.; *amide*, m.p. 107—108°). W. C. J. R.

Derivatives of 3 : 5-di-iodohippuric acid. B. K. Blount, J. C. L. Resuggan, and F. A. Robinson (*Quart. J. Pharm.*, 1942, **15**, 16—20).—3 : 5-*Di-iodo*-4-*hydroxyhippuric acid* (**I**), m.p. 223—224° [O-*Ac*, m.p. 205—206°, and O-*benzyl*, m.p. 216—218° (Et ester, m.p. 164—165°), derivatives], prepared from glycine and *p*-OAc·C_6H_4·COCl followed by hydrolysis and iodination, yields a very sol. Na_2 salt. When injected intravenously into rabbits there is 100% excretion (begins ~75 min. after injection; complete in ~2·5 hr.). The toxicity is 1·8 times as great as that of iodoxyl (**II**). 3 : 5-*Di-iodo*-4-*carboxymethoxyhippuric acid*, m.p. 227° (Et_2 ester, m.p. 112—113°), from $CH_2Cl·CO_2Et$ and the Et ester of (**I**) followed by hydrolysis, is nearly 1·4 times as toxic as (**II**) when tested on rats and nearly twice as toxic when tested on mice. J. N. A.

Alkanolamines. XI. Monoalkylamino-alcohols and their esters. C. B. Kremer and E. Waldman (*J. Amer. Chem. Soc.*, 1942, **64**, 1089—1090).—$NH_2·CMe_2·CH_2·OH$ and RBr in boiling EtOH give *β-ethyl-*, m.p. 75·5—76·5°, b.p. 162—163°, -n-, m.p. 59·5—60·5°, b.p. 183—185°, and -iso-*propyl-*, m.p. 43—45°, b.p. 165—166°, -n-, m.p. 69·5—70°, b.p. 195—196°, and -iso-*butyl-*, m.p. 51—52·5°, b.p. 185—186°, -n-, m.p. 60—60·5°, b.p. 216—217°, and -iso-*amyl-*, m.p. 76·5—77°, b.p. 205—207°, *-amino*iso*butyl alcohol*, converted by *p*-$NO_2·C_6H_4·COCl$ in C_5H_5N at 30—40° (not in alkali) into the p-*nitrobenzoates*, m.p. 206·5—207° (impure), 185—185·5°, 140—141° (impure), 163·5—164°, 165—166°, 151—151·5°, and 168—168·5°, respectively. In conc. HCl at +40—45° powdered Sn then gives the hygroscopic *p*-aminobenzoate hydrochlorides (not detailed). R. S. C.

Amidine salts of aminobenzoic acids.—See B., 1942, II, 280.

Dimorphism of amylcaine hydrochloride. H. R. Kreider and A. R. Menotti (*J. Amer. Chem. Soc.*, 1942, **64**, 1227—1228).—Dimorphic forms, m.p. 153·5° (corr.) and 176° (2 pseudomorphs), of *p*-$NH_2·C_6H_4·CO_2·[CH_2]_2·NH·C_5H_{11}$-*n*,HCl are described with photomicrographs. R. S. C.

Rearrangement of 3 : 5-dichloro-4-crotyloxybenzoic acid. D. S. Tarbell and J. W. Wilson (*J. Amer. Chem. Soc.*, 1942, **64**, 1066—1070; cf. A., 1942, II, 258).—Alkaline hydrolysis of 4 : 3 : 5 : 1-$OH·C_6H_2Cl_2·CO_2Et$ (**I**) (prep. from *p*-$OH·C_6H_4·CO_2Et$ by SO_2Cl_2 in 81% yield), m.p. (+H_2O) 108—116° (decomp.) and (anhyd.) 111—112°, gives the acid (89%), m.p. 268—269° (lit. 265°). (**I**) with, best (63%; 22% pure), CHMe:CH·CH_2Br and NaOH in boiling, aq. $COMe_2$ and subsequent hydrolysis (Claisen's alkali) gives 3 : 5-*dichloro*-4-*crotyloxybenzoic acid* (**II**), m.p. 150—152° [structure proved by oxidation by alkaline $KMnO_4$ to 2 : 6-*dichloro*-4-*carboxyphenoxyacetic acid* (78%), m.p. 248—250°, not obtained from (**I**) and $CH_2Br·CO_2Et$]. Rearrangement of (**II**) to 4 : 2 : 6 : 1-CHMe:CH·$CH_2·C_6H_2Cl_2$·OH (**III**) (61%) (*phenylurethane*, m.p. 149—150°) occurs without inversion at 165—175°, but in $NPhMe_2$ at 155° only decarboxylation occurs. 78% of 2 : 6 : 1-$C_6H_3Cl_2·OH$ is obtained from 4 : 3 : 5 : 1-$OH·C_6H_2Cl_2·CO_2H$ in $NPhMe_2$ at 155°, later 190°. 4 : 2 : 6 : 1-$C_6H_2Bu^aCl_2·OH$, b.p. 111—115°/3 mm. (*phenyl-*, m.p. 143—144°, and α-*naphthyl-urethane*, m.p. 142—143°), is obtained from (**III**) by H_2–PtO_2 in EtOH and by Clemmensen reduction of 3 : 5-*dichloro*-4-*hydroxybutyrophenone* (**IV**), m.p. 96—97°. 2 : 6-*Dichlorophenyl* n-*butyrate* [prep. by $(Pr^aCO)_2O$–C_5H_5N at 100°], b.p. 118—119°/3 mm., with $AlCl_3$ in $PhNO_2$ at room temp. gives 2 : 6 : 1-$C_6H_3Cl_2·OH$ (~57%) but at 140—150° (no solvent) gives (**IV**) (59%). 2 : 6-*Dichlorophenyl acetate*, b.p. 125—126°/17 mm., gives similarly 3 : 5-*dichloro*-4-*hydroxyacetophenone* (69%), m.p. 164—165·5°, converted by MgEtBr into *β*-3 : 5-*dichloro*-4-*hydroxyphenylbutan-β-ol* (56%), m.p. 116—117°, which with a trace of I at 185° gives 2 : 6-*dichloro*-4-(?)α-*methylpropenyl-* (88%), b.p. 161—163°/17 mm., and thence (H_2–PtO_2; EtOH) -4-sec.-*butyl-phenol*, m.p. 68—70° (*phenylurethane*, m.p. 100—101°). 2 : 6-*Dichlorophenyl allyl ether* (prep. by CH_2:CH·CH_2Br and K_2CO_3 in COMeEt), b.p. 89—90°/2 mm., at 193—200° (N_2) gives 2 : 6-*dichloro*-4-*allyl-* (~57%), m.p. 33—35°, b.p. 104—108°/3 mm., and 6-*chloro*-2-*allyl-phenol* (~10%) (**V**), b.p. 61—63°/1 mm. (α-*naphthylurethane*, m.p. 125—126°). o-*C_6H_4Cl allyl ether* (prep. in $COMe_2$), b.p. 108—110°/15 mm., at the b.p. gives 89% of (**V**). R. S. C.

***p*-Sulphonamidobenzamidine.**—See B., 1942, III, 189.

Attempted synthesis of homo*iso*vanillic acid. O. Hromatka (*Ber.*, 1942, **75**, [*B*], 123—131).—Attempts from *o*-$NO_2·C_6H_4·OMe$ and *o*-$C_6H_4Cl·OMe$ are described. 3 : 4 : 1-$NO_2·C_6H_3(OMe)·CH_2Cl$ is converted by KCN in aq. EtOH at 65—70° into 3-*nitro*-4-*methoxyphenylacetonitrile*, m.p. 86—87°, b.p. 175°/0·3 mm., reduced (H_2, Pd–C, MeOH at 19·5°) to 3-amino-4-methoxyphenylacetonitrile (**I**) (*hydrochloride*, m.p. 202°; picrate, m.p. 180°); attempts to diazotise the base were unsuccessful. (**I**) and 85% H_2SO_4 at 50° give 3-*nitro*-4-*methoxy-* (**II**), m.p. 155°, whereas at 95° the product is -4-*hydroxy-*, m.p. 162°, *-phenylacetamide*. (**II**) is converted by boiling aq. NaOH into 3-*nitro*-4-*methoxyphenylacetic acid* (**III**), m.p. 132°, reduced (as above) to the 3-NH_2-acid, m.p. 105°, which yields red resins and a small amount of *p*-$OMe·C_6H_4·CH_2·CO_2H$ when diazotised and boiled with H_2O. (**II**) is reduced to 3-*amino*-4-*methoxyphenylacetamide*, m.p. 164°. 2N-NaOMe–MeOH at 120° converts (**III**) into 2 : 2′-*dimethoxyazoxybenzene*-5 : 5′-*diacetic acid*, m.p. 195—196°. 4 : 3 : 1-$OMe·C_6H_3Cl·CH_2Cl$, m.p. 38° (obtained in 89·7% yield by saturating *o*-$C_6H_4Cl·OMe$ in an excess of 40% CH_2O with HCl at 96°), and KCN in boiling $Pr^{\beta}OH$ give 3-*chloro*-4-*methoxyphenylacetonitrile*, m.p. 55°, hydrolysed by KOH–H_2O–EtOH to the *acid* (**IV**), m.p. 98°, which is oxidised by $KMnO_4$ to 4 : 3 : 1-$OMe·C_6H_3Cl·CO_2H$, m.p. 213°. NaOMe in MeOH at 185° converts (**IV**), into 3-*chloro*-4-*hydroxyphenylacetic acid*, m.p. 107°. With KOH–NaOH at 220° (**IV**) gives 2 : 4 : 1-$OH·C_6H_3(OMe)·CH_2·CO_2H$, m.p. 130°, which when distilled affords 5-*methoxycoumaranone*, m.p. 56°, and with CH_2N_2 gives 2 : 4 : 1-$(OMe)_2C_6H_3·CH_2·CO_2H$. 3 : 3′-*Dichloro*-4 : 4′-*dimethoxydiphenylmethane*, m.p. 78°, is obtained from *o*-$C_6H_4Cl·OMe$, CH_2O, $ZnCl_2$, and HCl at 90°. H. W.

Phenylglutaric acids. III. αα-Diphenylglutaric acid. J. J. Trivedi, N. L. Phalnikar, and K. S. Nargund (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 135—136; cf. A., 1937, II, 195; 1938, II, 188).—$CHPh_2·CN$, I·$[CH_2]_2·CO_2Et$, and EtOH–NaOEt give after hydrolysis (20% NaOH at room temp.) *γ-cyano-γγ-diphenylbutyric acid*, m.p. 161—162°, hydrolysed (conc. HCl, 160—170°, 6 hr.) to αα-*diphenylglutaric acid*, m.p. 193—194° [*anhydride* (**I**), m.p. 142—143°; *monoanilide*, m.p. 208°; *mono*-p-*toluidide*, m.p. 168°]. (**I**) at 180—190° in dry NH_3 yields αα-*diphenylglutarimide*, m.p. 158—159°. W. C. J. R.

***cyclo*Hexane series. VI. Stereoisomeric forms of 4- and 3-methyl-*cyclo*hexane-1 : 1-dicarboxylic acid, and conclusive chemical evidence for the multiplanar *cyclo*hexane ring.** R. D. Desai, R. F. Hunter, and G. S. Sahariya (*Proc. Indian Acad. Sci.*, 1942, **15**, **A**, 168—172).—1-Carboxy-4-methyl-1-*cyclo*hexylacetic acid-*A*, m.p. 173°, and *-B*, m.p. 137°, with successively PCl_5, Br first at room temp. (sunlight) and then at 50—60°, and HCO_2H, yield the *-α-bromoacetic acid*-A, m.p. 152° [with the *β-lactone*, m.p. 110° (previous sintering) (*NH_2Ph* salt +H_2O, m.p. 160°), of (**I**) (below)], and -B, m.p. 132°, respectively, hydrolysed (2N-aq. Na_2CO_3) to the -1-*carboxylic*-1-*glycollic acid*-A (**I**), m.p. 134°, and -B, m.p. 138°, respectively, oxidised (alkaline $KMnO_4$) to the -1 : 1-*dicarboxylic acid*-A, m.p. 170° (decomp.), and -B, m.p. 175° (decomp.), respectively. Similarly 1-carboxy-3-methyl-1-*cyclo*hexylacetic acid-*A*, m.p. 163°, and *-B*, m.p. 108—109°, yield the *-α-bromoacetic acid*-A, m.p. 142°, and -B, m.p. 155°, respectively, -1-*carboxylic*-1-*glycollic acid*-A, m.p. 166°, and -B, m.p. 134°, respectively, and -1 : 1-*dicarboxylic acid*-A, m.p. 171—172° (decomp.), and -B, m.p. 185° (decomp.), respectively. The existence of the above pairs of stereoisomeric 1 : 1-dicarboxylic acids supplies the first proof of the multiplanar forms of the *cyclo*hexane ring. A. Li.

Sulphur studies. XVIII. Sulphonium derivatives from *p*-phenylphenacyl bromide. R. W. Bost and H. C. Schultze (*J. Amer. Chem. Soc.*, 1942, **64**, 1165—1167; cf. A., 1941, II, 332).—*p*-$C_6H_4Ph·CO·CH_2Br$ (**I**) and Alk_2S, in, best, boiling abs. MeOH give p-*phenylphenacyldialkylsulphonium bromides* (*A*), which with the Ag salts of strong acids give the derived other sulphonium salts. Sulphonium salts of weak acids (AcOH, BzOH, *o*-$OH·C_6H_4·CO_2H$, *p*-$NH_2·C_6H_4·SO_2·NH_2$) cannot be isolated and with H_2S give the sulphonium H sulphide, which decomposes to give p-*phenylphenacyl mercaptan*, m.p. 109° (2 : 4-dinitrophenylhydrazone, m.p. 159°), and R_2S. (*A*) and the derived *nitrates*, *H sulphates*, and *sulphanilates*, respectively, are described in which the alkyl are *Me_2*, m.p. 148°, 136°, —, and 166° (and the normal *sulphate*, m.p. 148°), *Et_2*, m.p. 131°, 125°, 157°, and 139°, *Pr^{α}_2*, m.p. 117°, 118°, 152°, and an oil, *Bu^{α}_2*, m.p. 96—107°, 138°, 172°, and an oil, *Me Et*, m.p. 139°, 134°, 155°, and 163°, *Me Pr^{α}*, m.p. 131°, 121°, an oil, and 158°, *Me Bu^{α}*, m.p. 119°, 137°, 168°, and 146° (and the *benzenesulphonate*, m.p. 129—134°), and *diallyl*, m.p. 72°, —, —, —. COPh·CH_2Br and $MeSBu^{\alpha}$ in abs. MeOH give SMe_2BuBr. *p*-Phenylphenacyldi-*n-* and *-iso*-amylsulphonium bromides are oils. R. S. C.

Constitution of natural tannins. VIII. Colouring matters derived from anthracene-9-aldehyde. A. Russell and W. B. Happoldt, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 1101—1103; cf. A., 1941, II, 173).—9-Anthraldehyde (improved prep.) and COArMe in HCl–EtOAc at room temp. give 27—71% of *Ph*, m.p. 122—123°, o-*benzoyloxy-*, m.p. 151°, o-, m.p. 159—160°, m-, m.p. 202°, and p-*hydroxy-*, m.p. 241—242°, 2 : 6-, m.p. 224°, and 2 : 5-*dibenzoyloxy-*, m.p. 171°, 2 : 5-, m.p. 146°, and 2 : 4-*diacetoxy-*, m.p. 188°, 2 : 5-, m.p. 228·5°, and 2 : 4-*dihydroxy-* (prep. in boiling KOH–MeOH–N_2), m.p. 199°, 2 : 3 : 4-*tribenzoyloxy-*, m.p. 161—162°, 2 : 4-, m.p. 139°, and 2 : 6-*dimethoxyphenyl*, m.p. 202°, p-*diphenylyl*, m.p. 212—213°, and *β-*$C_{10}H_7$ *β*-9-

anthranylvinyl ketone, m.p. 163°. 2 : 4 : 1-$(OH)_2C_6H_3$·COMe gives *7-hydroxy-2-9′-anthranylbenzopyrone* (59%), m.p. 212—220°. R. S. C.

***anti*-Phenyl phenylthiolmethyl ketoxime. Attempted synthesis of benzo-*m*-thiazine derivatives.** E. Vinkler (*J. pr. Chem.*, 1941, [ii], **159**, 115—120).—SPh·CH_2·COPh affords the anti-*oxime* (**I**), m.p. 81—82°, converted (PCl_5–Et_2O) into SPh·CH_2·CO·NHPh, m.p. 82—83° (also obtained from SPh·CH_2·CO_2H and NH_2Ph at 150°). (**I**) could not be converted into the *syn*-form. A. T. P.

Condensation of *o*-anisylsuccinic anhydride with *o*- and *m*-tolyl methyl ethers. B. S. Mehta, K. V. Bokil, and K. S. Nargund (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 137—140; cf. A., 1940, II, 132).—*o*-Anisylsuccinic anhydride (**I**), *o*-C_6H_4Me·OMe, and $AlCl_3$ in $PhNO_2$ or $C_2H_2Cl_4$ give *β-6-methoxy*-m-*toluoyl*-α-*o-anisylpropionic acid* (44—54%), m.p. 183° [with MeOH–HCl gives a pyrylium compound, m.p. >300°; *Me* (via Ag salt), m.p. 101°, and *Et* ester, m.p. 63—65°], and *β-6-methoxy*-m-*toluoyl*-*β*-*o-anisylpropionic acid* (42—49%), m.p. 140—141° (*semicarbazone*, m.p. 200°; *Me*, m.p. 113°, and *Et* ester, m.p. 93°). 4 : 3 : 1-OMe·C_6H_3Me·COMe, *o*-OMe·C_6H_4·CHO (**II**), and 50% aq. NaOH afford 6-*methoxy*-m-*tolyl* o-*methoxystyryl ketone*, m.p. 79°, which did not react with KCN or Br. (**I**) similarly condenses with *m*-C_6H_4Me·OMe to give *β-5-methoxy*-o-*toluoyl*-α-*o-anisylpropionic acid* (**III**) (58—60%), m.p. 151—152° (*Me*, m.p. 115°, and *Et* ester, m.p. 122°), and *β-5-methoxy*-o-*toluoyl*-*β*-*o-anisylpropionic acid* (20—27%), m.p. 125°. *5-Methoxy*-o-*tolyl* o-*methoxystyryl ketone*, b.p. 210—215°/11 mm. [from 4 : 2 : 1-OMe·C_6H_3Me·COMe and (**II**)], with KCN gives a product hydrolysed to (**III**). W. C. J. R.

Self-condensation of acetyl*cyclo*hexene. E. R. H. Jones and H. P. Koch (*J.C.S.*, 1942, 393—395).—The two dimerides, m.p. 205° [*mono-oxime*, m.p. 254° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 293°] and new m.p. 130° [*mono-oxime*, m.p. ~250° (decomp.); 2 : 4-*dinitrophenylhydrazone*, m.p. 212—213°], formed from 1-acetyl*cyclo*hexene by $NaNH_2$–Et_2O (cf. Rapson *et al.*, A., 1935, 1498) are probably stereoisomeric α- and *β-9-keto*-12-*acetyltetradecahydrophenanthrene*, respectively. They both yield (Se at 300°) phenanthrene and show no high-intensity absorption in the ultra-violet. A third condensation product is probably 1-*keto*-3-$\Delta^{1'}$-cyclo*hexenyl*-Δ^2-*octahydronaphthalene*, m.p. 85° [*oxime*, m.p. 232° (decomp.); *semicarbazone*, m.p. 213°; 2 : 4-*dinitrophenylhydrazone*, m.p. 228°], dehydrogenated by Pd–C at 340° (in CO_2) to 2-$C_{10}H_7$Ph. 1-Acetyl-2-methyl*cyclo*hexene does not undergo self-condensation with $NaNH_2$–Et_2O. A. T. P.

Antihæmorrhagic activity of sulphonated derivatives of 2-methylnaphthalene. B. R. Baker, T. H. Davies, L. McElroy, and G. H. Carlson (*J. Amer. Chem. Soc.*, 1942, **64**, 1096—1101).—Heating 1 : 2 : 4-O:$C_{10}H_5$Me:O with aq. $NaHSO_3$ or $KHSO_3$ at 100° and then cooling at 0° and adding $COMe_2$ ppts. the biologically active *Na* or *K* salt (**I**), respectively, of the 1 : 1 additive compound. Concn. of the mother-liquor and addition of KCl yields *K* 2-*methyl*-1 : 4-*naphthaquinol*-3-*sulphonate* (**II**), which has <0·1 times the biological potency of (**I**). (**I**) and (**II**) are differentiated by formation of the corresponding S-*benzylthiuronium* salts, m.p. 127—129° (decomp.) and 138—139° (decomp.), respectively. With $K_2Cr_2O_7$–H_2SO_4–H_2O at 25°, (**II**) or the initial crude reaction product gives readily *K* (**III**) and thence S-*benzylthiuronium* 2-*methyl*-1 : 4-*naphthaquinone*-3-*sulphonate*, m.p. 156—157°; the *Na* salt is similarly obtained. (**III**) is reconverted into (**II**) by $Na_2S_2O_4$ and with alkaline $KMnO_4$ gives *o*-$C_6H_4(CO_2H)_2$ (**IV**). The structure of (**II**), (**III**), etc. is proved as follows. 2 : 1 : 4-$C_{10}H_5$Me$(OAc)_2$ (**V**) with $ClSO_3H$ in $CHCl_3$ at room temp. gives *Na* 2-*methyl*-1 : 4-*naphthaquinol*-3-*sulphonate diacetate*, m.p. 148—150° (decomp.), oxidised by CrO_3–AcOH–H_2O–KCl to (**III**) and converted by HNO_3–H_2O into 3-*nitro*-2-*methyl*-1 : 4-*naphthaquinone*, m.p. 124·5—125·8°. $KMnO_4$ oxidises this to (**IV**), and H_2–PtO_2 in AcOH yields 3-amino-2-methyl-1 : 4-naphthaquinol, isolated as *hydrochloride*, m.p. 205—207° (decomp.), or *triacetate* (**VI**) (prep. at 80—100°), m.p. 214—215° (with boiling Ac_2O–NaOAc gives the *tetra-acetate*, m.p. 173—174·5°), and oxidised by $FeCl_3$–HCl–H_2O to 3-*amino*-2-*methyl*-1 : 4-*naphthaquinone*, m.p. 162—162·5°, which in hot 10% NaOH gives phthiocol. With NH_3 in aq. MeOH at 45°, (**V**) gives 2-*methyl*-1 : 4-*naphthaquinol* (*mono*-)*acetate*, m.p. 124·5—125·8°, the 3-p-*nitrobenzeneazo*-derivative, m.p. 274—276°, of which with $KMnO_4$ gives (**IV**) and with H_2–catalyst in AcOH and then Ac_2O–NaOAc at 100° gives (**VI**) and thence (boiling 10% NaOH–air) phthiocol. The stability of (**I**) to $K_3Fe(CN)_6$ etc. greatly exceeds that of (**II**). The 3-sulphonate is formed by way of the active additive compound, since the yield of (**III**) and the amount of reducible material (potentiometric) increase if the initial heating is prolonged. The rate of conversion (followed by titration with 2 : 6-dichlorophenol-indophenol) is decreased by increase in acidity. The bearing of the results on the use of commercial preps. ("Hykinone") is noted. R. S. C.

Sulphonation of 1-aminoanthraquinone compounds.—See B., 1942, II, 280.

IV.—STEROLS AND STEROID SAPOGENINS.

7-Benzoyloxysterols and their use in preparation of 7-dehydrosterols. O. Wintersteiner and W. L. Ruigh (*J. Amer. Chem. Soc.*, 1942, **64**, 1177—1179).—7(α)-Benzoyloxycholesteryl benzoate with NaOMe–MeOH–C_6H_6 at room temp. gives, after chromatography, 7(α)-*benzoyloxycholesterol* (**I**), m.p. 110—115°, $[\alpha]_D^{24}$ +111° in $CHCl_3$ [absorption max. at 230 (ε 12,750) and 272 mμ. (ε 740); 3 : 5-*dinitrobenzoate*, m.p. 162—163°, $[\alpha]_D^{24}$ +80·5° in $CHCl_3$; p-*toluenesulphonate*, m.p. varies, 90° to 100° (decomp.), with KOAc–MeOH gives an impure compound, m.p. 153·5—155·5°; no digitonide]. Pyrolysis (2 mm.) or boiling in $NPhMe_2$–CO_2 converts (**I**) into 7-dehydrocholesterol, m.p. 142·5—143·5°, $[\alpha]_D^{26}$ −121° in $CHCl_3$ (3 : 5-dinitrobenzoate, m.p. 209·5—210·5°, $[\alpha]_D^{26}$ −38·3° in $CHCl_3$) (cf. lit.). 7(α)-Benzoyloxystigmasteryl benzoate, m.p. 183·5—185° (lit. 156—158°, 184—186°), with NaOMe–MeOH–C_6H_6 at 23—25° gives 7(α)-*benzoyloxystigmasterol*, m.p. 154·5—156·5°, resolidifies, remelts at 193°, $[\alpha]_D^{24}$ +100·8° in $CHCl_3$ (no digitonide; 3 : 5-*dinitrobenzoate*, m.p. 150·5—152·5°), converted in boiling $NPhMe_2$ into 7-dehydrostigmasterol, m.p. 150—152·5°, $[\alpha]_D^{27}$ −104·0° in $CHCl_3$, −109·8° in C_6H_6 [absorption max. at 282 mμ. (ε 10,800); *benzoate*, m.p. 178·5—180°, $[\alpha]_D^{26}$ −48·5° in $CHCl_3$]. R. S. C.

Sterols. CXLI. 3(α) : 11 : 12-Trihydroxycholanic acid. R. E. Marker, A. C. Shabica, E. M. Jones, H. M. Crooks, jun., and E. L. Wittbecker (*J. Amer. Chem. Soc.*, 1942, **64**, 1228—1229).—Contrary to Longwell *et al.* (A., 1940, II, 95), 3(α) : 11-dihydroxy-12-ketocholanic acid with N_2H_4,H_2O, NaOEt, and EtOH at 200° gives 3(α) : 11 : 12-*trihydroxycholanic acid*, m.p. 136° (decomp.), converted by CrO_3–AcOH and then Hg–Zn–HCl into neolithobilianic acid (**I**). 11-Hydroxy-12-ketocholanic acid (**II**) gives similarly 11 : 12-dihydroxycholanic acid, m.p. 204—208°, and thence (**I**) [also obtained directly from (**II**) by CrO_3–AcOH]. R. S. C.

Sterol group. XLIV. Oxidation of phytosterols with the Oppenauer reagent. E. R. H. Jones, P. A. Wilkinson, and (in part) R. H. Kerlogue (*J.C.S.*, 1942, 391—393; cf. A., 1941, II, 251).—Cholesterol is oxidised [$Al(OBu^t)_3$–$COMe_2$–C_6H_6] to cholestenone (2 : 4-dinitrophenylhydrazone, m.p. 233°). Fucosterol yields *fucostadienone* (50%), m.p. 94—94·5° [*semicarbazone*, m.p. 238° (decomp.); *oxime*, m.p. 166—167°; 2 : 4-*dinitrophenylhydrazone*, m.p. 237°], and stigmasterol affords stigmastadienone (58%), m.p. 124·5—125° [*oxime*, m.p. 187—188°; 2 : 4-*dinitrophenylhydrazone*, m.p. 244—245° (decomp.); semicarbazone, new m.p. 238—239°]. β-Sitosterol (**I**), m.p. 136—137° [obtained from its acetate, m.p. 125° (16 crystallisations from EtOAc), and KOH–EtOH], is oxidised similarly to sitostenone (15%), m.p. 83—84° (2 : 4-*dinitrophenylhydrazone*, m.p. 247—248°), and a ketone (~10%), m.p. 143—145° (2 : 4-*dinitrophenylhydrazone*, m.p. 208—209°), probably a mixture. Absorption spectra of the ketones and their derivatives are in accordance with expectations. It is doubtful if (**I**) as described in the literature is a homogeneous substance. A. T. P.

Enolic ethers of keto*cyclo*pentanopolyhydrophenanthrenes.—See B., 1942, III, 189.

Diazoprogesterone.—See B., 1942, III, 189.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Syntheses in the camphor and terpene group. G. Komppa (*Ber.*, 1942, **75**, [*A*], 1—13).—A lecture. H. W.

Influence of anhydride or lactone formation on the rotatory power of the diacids or hydroxy-acids derived from *d*-camphor. J. Vène (*Compt. rend.*, 1941, **213**, 842—843).—[α] of all known lactones or anhydrides (except β-campholide) having the 1 : 2 : 2-trimethyl-*cyclo*pentane nucleus (whether halogenated or not), derived from *d*-camphor, is negative, that of the corresponding OH- or dibasic acids positive. A. Li.

Alterations in molecular structure during chemical reactions. V. Neomenthol and phosphorus pentachloride. W. Hückel and K. Kümmerle (*Ber.*, 1942, **75**, [*B*], 115—120).—The action of PCl_5 on *d*- and *dl*-neomenthol (**I**) under conditions similar to those used for menthol (**II**) (A., 1937, II, 157) invariably gives menthene in amount which is variable and very dependent on slight variations in experimental technique. Chlorides are formed in considerable amount, mainly racemised neomenthyl chloride and *tert.*-4-chloromenthane (**III**) (ratio ~3 : 2) with a little *l*-menthyl and *d*-neomenthyl chloride (~1 : 1). A part of (**III**) is isolated as such whereas the other part changes to *p*-menthan-4-ol; two 4-chloromenthanes hydrolysed with differing readiness must therefore be formed, of which only one stereoisomeride is isolated. Substitution of OH by Cl in (**I**) is accompanied to a considerable extent by migration of the halogen to the *tert.* position at $C_{(4)}$. The almost complete racemisation of the *sec.* chloride proves that Cl in the *sec.* position at $C_{(3)}$ in the reaction product is not a result of simple substitution. In general, substitution of OH by Cl in (**I**) does not proceed in the same manner as in (**II**) and resembles the change with aliphatic alcohols. H. W.

Sesquiterpenes. LII. Degradation of dihydroguaiol by chromic acid. Preparation of 1 : 4 : 7-trimethylazulene. P. A Plattner and G. Magyar (*Helv. Chim. Acta*, 1942, **25**, 581—589).—Dihydroguaiol is oxidised by CrO_3 in AcOH at 70° to 2 : 8-dimethyldi*cyclo*-[0 : 3 : 5]-

decan-5-one (I), $[\alpha]_D$ −85·8° in EtOH (semicarbazone, m.p. 206°, $[\alpha]_D$ −80·5° in AcOH), and an *acid* (II), probably $CHMe<^{CH_2—CH_2}_{CH(CO_2H)}>CH\cdot CHMe\cdot[CH_2]_2\cdot CO_2H$, m.p. 186—187°, $[\alpha]_D$ ±0° in EtOH, +1·5° in 0·3N-KOH–EtOH (*Me*$_2$ ester, $[\alpha]_D$ −6·2° in EtOH), also obtained by ozonisation of *benzylidene*-2 : 8-*dimethyldi*cyclo-[0 : 3 : 5]-*decan*-5-*one*, m.p. 149°, $[\alpha]_D$ +124·1° in EtOH, prepared by the action of NaOH and PhCHO in EtOH on (I). Oxidation (Br–KOH in dioxan) of (I) gives a *Br*$_2$-derivative, m.p. 97—98°, and (II). Guaiazulene is obtained by treatment of (II) with $MgPr^\beta Br$ followed by dehydrogenation of the product by S at 200°/650 mm. (I) and MgMeI in Et_2O give 2 : 5 : 8-*trimethyldi*cyclo-[0 : 3 : 5]-*decan*-5-*ol*, m.p. 83°, $[\alpha]_D$ −10° in hexane, dehydrated by $KHSO_4$ at 180°/600 mm. to 2 : 5 : 8-*trimethyldi*cyclo-[0 : 3 : 5]-*decene*, b.p. 110—114°/12 mm., which is dehydrogenated by S at 200°/600 mm. to 1 : 4 : 7-trimethylazulene [additive compound, m.p. 177—178°, with 1 : 3 : 5-$C_6H_3(NO_2)_3$]. M.p. are corr. (See also A., 1942, II, 280.) H. W.

VI.—HETEROCYCLIC.

Furoanilides.—See B., 1942, II, 272.

***dl*-Δ^3-Dehydro-α-tocopherol.**—See B., 1942, III, 189.

Chemistry of the lignan group of natural products. R. D. Haworth (*J.C.S.*, 1942, 448—456).—A lecture. F. R. S.

1 : 3-Dioxans.—See B., 1942, II, 255.

Synthesis of ethyl 1-methylpyrrolidine-2-acetate. F. E. King, J. W. Clifton, and H. T. Openshaw (*J.C.S.*, 1942, 422—424).— *Et*$_3$ ε-*phenoxypentane*-αββ-*tricarboxylate*, b.p. 203—205°/1 mm., obtained from Et ethanetricarboxylate and $OPh\cdot[CH_2]_3\cdot Br$ with NaOEt–EtOH, is hydrolysed (KOH) to the *acid*, m.p. 132—134°, which is decarboxylated at 150° to the *αβ-dicarboxylic acid* (I), m.p. 153° (*Br*$_2$-derivative, m.p. 145—146°). HBr and (I) give ε-*bromopentane*-αβ-*dicarboxylic acid*, m.p. 91—92°, which does not afford a recognisable product on treatment with Br. NH_3 and (I) yield the NH_4 salt, which on heating is converted into ε-*phenoxypentane*-αβ-*dicarboxylimide*, m.p. 85—86°, which with NaOBr gives a mixture containing ε-*phenoxy*-Δ$^\alpha$-*hexenoic acid*, m.p. 86°, obtained in purer form from $CH_2(CO_2H)_2$ and γ-phenoxybutyronitrile (*semicarbazone*, m.p. 118°). This acid and HBr–P–AcOH afford βε-*dibromo*-n-*hexoic acid*, b.p. 154°/1 mm., which with NH_2Me–MeOH forms Et 1-methylpyrrolidine-2-acetate, converted by Na–PhMe–Et_2O followed by H_2SO_4 and picric acid into *Et* β-*keto*-αγ-*di*-(1-*methyl*-2-*pyrrolidyl*)*butyrate dipicrate*, m.p. 155—157° (decomp.), and not cuskhygrine dipicrate. F. R. S.

2 : 3 : 6-Triaminopyridine.—See B., 1942, II, 255.

Arylazopyridines.—See B., 1942, III, 190.

Synthesis of 2-methylpyrrolizidine. G. R. Clemo and T. A. Melrose (*J.C.S.*, 1942, 424—426).—3-Keto-4 : 5-dihydrodi-(1 : 2)-pyrrole with Zn–MeI gives a condensation *product*, m.p. 209° (by elimination of H_2O from 2 mols of ketone), and is reduced (Na–Hg) to the *pinacol*, m.p. 183—184°. CH_2:$CMe\cdot CO_2Me$ and HBr–AcOH yield *Me* β-*bromoisobutyrate*, b.p. 75°/22 mm. 5-Methyl-4 : 5-dihydrouracil is hydrolysed (HCl) to β-*carbethoxy*-n-*propylamine*, b.p. 71°/13 mm. (*picrate*, m.p. 108—109°), which with $CH_2Cl\cdot CO_2Et$–NaOAc affords *carbethoxymethyl*-β-*carbethoxy*-n-*propylamine*, b.p. 110°/1 mm. (picrolonate, m.p. 137—138°), converted by K–PhMe into *Et* 3-*hydroxy*-4-*methylpyrrole*-2-*acetate*, m.p. 85° (p-*nitrobenzoyl* derivative, m.p. 152°). Reduction (H_2–PtO_2) of Et pyrrole-2-acetate gives *Et pyrrolidine*-2-*acetate*, b.p. 110°/27 mm. (*picrolonate*, m.p. 146°), which with $CH_2Br\cdot CO_2Et$ yields the -1 : 2-*diacetate*, b.p. 125°/1 mm. This ester and K form 2-*ketopyrrolizidine*, b.p. 78°/1 mm. (*picrolonate*, m.p. 212—213°), which with Mg–MeI gives 2-*hydroxy*-2-*methylpyrrolizidine*, b.p. 95°/1 mm. (*picrolonate*, m.p. 198°). The carbinol and PCl_5 afford *dehydro*-2-*hydroxy*-2-*methylpyrrolizidine* (*picrolonate*, m.p. 169—170°), which is reduced (H_2–PtO_2) to 2-methylpyrrolizidine, b.p. 62°/25 mm., the *picrate*, m.p. 169—170°, of which is not identical with that obtained by Menschikoff (A., 1936, 1123). F. R. S.

Preparation of 8-hydroxyquinoline. F. E. King and J. A. Sherred (*J.C.S.*, 1942, 415—416).—8-Methoxyquinoline has been prepared by the Skraup reaction using As_2O_5 and is readily demethylated with boiling HBr. F. R. S.

Reaction of 4-chloroquinaldines and of 2-chlorolepidines with ammonia, and the preparation of the corresponding phenyl esters. O. G. Backeberg and J. L. C. Marais (*J.C.S.*, 1942, 381—383).—By passing NH_3 into a solution of 4-chloro-quinaldine or -quinoline in PhOH, 4-*amino*-6-, m.p. 209°, and -8-*methoxyquinaldine*, m.p. 233°, are formed, and these are also obtained by reduction of 4-*benzeneazo*-6-, m.p. 73°, and -8-*methoxyquinaldine*, m.p. 130°, respectively. By using the chlorolepidines in the same reaction, only 10% yields of the 2-aminolepidines are obtained and the products are mainly the Ph ethers, which are formed in theoretical yield in absence of NH_3. The following are described : 4-phenoxyquinoline [*picrate*, m.p. 179°; *platinichloride*, m.p. 220° (decomp.)]; 4-*phenoxy*-, m.p. 71·5°, 4-*phenoxy*-6-, m.p. 112°, and -8-*methoxy*-, m.p. 147°, -6-, m.p. 121°, and -8-*ethoxy-quinaldine*, m.p. 100°; 2-*phenoxy*-, m.p. 48°, 2-*phenoxy*-6-*methoxy*-, m.p. 70°, and -6-*ethoxy-lepidine*, m.p. 95°. When the chlorolepidines are heated (sealed tube) with $ZnCl_2,2NH_3$, the corresponding 2-*amino*-6-*methoxy*-, m.p. 174°, and -*ethoxy-lepidine*, m.p. 207°, are formed. Oxidation ($FeCl_3$) of the crude NHPh·NH-compound from the chlorolepidines gives 2-*benzeneazo*-6-*methoxy*-, m.p. 142°, and -6-*ethoxy-lepidine*, m.p. 162°. F. R. S.

Antiplasmodial action and chemical constitution. V. Carbinolamines derived from 6-methoxyquinoline. H. King and T. S. Work (*J.C.S.*, 1942, 401—404).—By the action of the appropriate alkyl halide on benzylhexylamine and removal of CH_2Ph by reduction (H_2–AcOH–PtO_2) the following are obtained : *benzyl*-n-*butyl*-, b.p. 170°/18 mm., n-*butyl*-, b.p. 201°/738 mm. (*hydrochloride*, m.p. 268°), *benzyl*-n-*amyl*-, b.p. 175—177°/15 mm., n-*amyl*-, b.p. 108°/15 mm. (*hydrochloride*, m.p. 275—276°), *benzyl*-n-*propyl*-, b.p. 155°/15 mm., n-*propyl*-, b.p. 171—181°/753 mm. (*hydrochloride*, m.p. 243°), *benzylethyl*-, b.p. 145°/13 mm., and *ethyl-hexylamine*, b.p. 158°/743 mm. (*hydrochloride*, m.p. 191°). Similarly prepared are *benzyl*-n-, b.p. 179°/12 mm. (*hydrochloride*, m.p. 199—200°), *benzyldi*-, b.p. 240°/12 mm., *benzyl*-n-*propyl*-, b.p. 185°/13 mm., *propyl*-, b.p. 119°/14 mm. (*hydrochloride*, m.p. 237°), *benzylethyl*-, b.p. 178°/11 mm. (*benzyldiethylnonylammonium iodide*, m.p. 64—65°), and *ethyl-nonylamine*, b.p. 103°/14 mm. (*hydrochloride*, m.p. 200—201°). Benzylnonylamine and MeI give *benzyldimethylnonylammonium iodide*, m.p. 89°, converted into the hydroxide and hydrosulphide, which in solution under reduced pressure affords *dimethylnonylamine*, b.p. 209°/741 mm. (*methiodide*, m.p. 170°). Nonyl iodide and NH_2Me in MeOH yield some *methyl*- (I), b.p. 95°/14 mm. (*hydrochloride*, m.p. 180—181°), but mainly *methyldi-nonylamine*, b.p. 190—192°/15 mm. Nonylamine and PhCHO give *benzylidenenonylamine*, b.p. 179°/14 mm., which with MeI, followed by 90% EtOH and HCl, forms (I). Condensation of the appropriate amine with 6-methoxy-4-quinolyl CH_2Br ketone hydrobromide followed by reduction gives *ethyl*-(*dipicrate*, m.p. 170°, *propyl*- (*dipicrate*, m.p. 169°), and *butyl-hexyl*-(*dipicrate*, m.p. 158—159°), and *methylnonyl-aminomethyl*- (*dipicrate*, m.p. 151°), and 2′ : 2′ : 6′-*trimethylpiperidinomethyl*-6-*methoxy*-4-*quinolylcarbinol* (*dipicrate*, m.p. 214°). The carbinolamines are inactive when tested on bird-malaria in canaries. F. R. S.

Synthesis of amines from amides through the amidodichlorides. T. S. Work (*J.C.S.*, 1942, 429—432).—*Cinchoninanilide*, m.p. 161—162°, prepared from cinchoninic acid, $SOCl_2$, and NH_2Ph, with PCl_5 followed by reduction ($SnCl_2$), gives N-*phenyl-lepidylamine* (I), m.p. 121°, and not the expected quinoline-4-aldehyde (Sonn–Müller reaction). Similarly, *cinchoninomethylamide*, m.p. 111°, affords N-*methyl-lepidylamine dihydrochloride*, m.p. 215—220° (decomp.). *Cinchoninodiethylamide*, b.p. 180°/2 mm. (*picrate*, m.p. 189°), does not undergo the reaction. 6-*Chlorocinchoninanilide*, m.p. 205°, with PCl_5 in $CHCl_3$ gives a mixture of the *hydrochloride* and an oil, converted by boiling NH_2Ph into NN-*diphenyl*-6-*chloro*-4-*quinolylamidine*, m.p. 207°. The hydrochloride and PCl_5 in $CHCl_3$ give an oil, which with CS_2 forms unstable orange needles (6-chlorocinchoninanilide amidodichloride?), and is reduced ($SnCl_2$) to N-*phenyl*-6-*chlorolepidylamine*, m.p. 129° (*nitrosamine*, m.p. 131°). *Quinoline*-4-*aldehyde anil*, m.p. 85°, is reduced ($SnCl_2$) to (I). *Nicotinethylamide*, m.p. 57°, with PCl_5 followed by $SnCl_2$ yields a mixture of pyridine-3-aldehyde and 3-N-*ethylaminomethylpyridine* (*platinichloride*; *picrate*, m.p. 207°). The mechanism of the reactions is discussed. F. R. S.

Antiplasmodial action and chemical constitution. VI. Compounds related to lepidylamine. T. S. Work (*J.C.S.*, 1942, 426—429).—Condensation of the appropriate aldehyde with diethyl-δ-aminoamylamine (I), followed by reduction (H_2–Pd–C), gives α-*diethylamino*-δ-*amyl-benzylamine*, b.p. 187—189°/25 mm., -p-*methoxy*-, b.p. 218°/17 mm., and -m-*amino-benzylamine*, b.p. 184—186°/25 mm., and -*lepidylamine* (dipicrate, m.p. 147—148°). Conversion of the cinchoninamide of δ-amino-α-diethylaminopentane by PCl_5 into the amidodichloride followed by reduction with $SnCl_2$ leads to the formation of the appropriate quinoline polyamines. Acetylsulphanilyl chloride (II) and lepidylamine followed by hydrolysis (NaOH) give N^1-*lepidylsulphanilamide*, m.p. 194°; N^1-(6-*methoxylepidyl*)*sulphanilamide*, m.p. 194° (N^4-*Ac* derivative, m.p. 215°), is similarly prepared. α-*Diethylamino*-δ-*amyl*-6-*methoxylepidylamine* (*tripicrate*, m.p. 87—88°) is prepared from quininic acid. ζ-*Diethylaminohexanol*, b.p. 96—99°/2 mm., prepared from hexamethylene chlorohydrin and $NHEt_2$, with $SOCl_2$ gives *diethylamino*-ω-*chlorohexane*, b.p. 118—120°/19 mm., which does not condense successfully with lepidylamine. 5-Chloroisatin and $AcCO_2H$ afford 6-*chloroquinoline*-2 : 4-*dicarboxylic acid*, m.p. ~250° (decomp.), which is partly decarboxylated (boiling $PhNO_2$) to 6-*chlorocinchoninic acid* (III), m.p. 302°, the *Me* ester, m.p. 79·5°, of which yields the *amide*, m.p. 244°, converted (P_2O_5) into the *nitrile*, m.p. 164°, which is reduced (H_2–PtO_2–HCl) to 6-*chloro*-4-*aminomethylquinoline*, m.p. 90° [*dihydrochloride*, m.p. ~250° (decomp.)]. 6-Chlorolepidylamine and (II) give N^4-*acetyl*-N^1-(6-*chlorolepidyl*)*sulphanilamide*, m.p. 194°, hydrolysed (NaOH) to the N^1-*compound*, m.p. 200°. The acid chloride hydrochloride of (III) with (I) affords the 6-*chlorocinchonin-*

amide of *diethyl-δ-aminoamylamine*, m.p. 99°, which after conversion into the amidodichloride followed by reduction ($SnCl_2$) leads to *α-diethylamino-δ-amyl-6-chlorolepidylamine* (picrate, m.p. 97—99°). None of the polyamines containing the quinoline nucleus and none of the sulphonamides showed any antiplasmodial action. F. R. S.

Chemotherapeutic studies in the acridine series. IX. Chloroaminoaeridines. F. R. Bradbury and W. H. Linnell (*J.C.S.*, 1942, 377—381).—4 : 2 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}CO_2Na$ and *m*-$C_6H_4Cl{\cdot}NH_2$ (Na_2CO_3–Cu–*n*-BuOH) give *3′-chloro-5-nitrodiphenylamine-2-carboxylic acid*, m.p. 221—222°, which with $POCl_3$ followed by HCl affords a mixture of chloronitroacridones, reduced ($SnCl_2$–HCl) to the corresponding NH_2-compounds, further reduced (Na–Hg) to 6-, m.p. 179—180°, and *8-chloro-2-aminoacridine* (**I**), m.p. 220—221°. 2 : 4 : 1-$(NO_2)C_6H_3{\cdot}CHO$, PhCl, and H_2SO_4 yield *4-nitro*-C-(*9-chlorophenyl*)-*anthranil* (**II**), m.p. 215°, and *8-chloro-2-nitro-10-hydroxyacridone*, m.p. 200° (*-10-OMe*-derivative, decomp. 241°); with $NaNO_2$–H_2SO_4 (**II**) gives 8-chloro-2-nitroacridone (also obtained if the original condensation be carried out in presence of $NaNO_2$), reduced ($SnCl_2$–HCl) to (**I**). 5 : 2 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}CO_2K$ and *m*-$C_6H_4Cl{\cdot}NH_2$ (K_2CO_3–Cu–*n*-BuOH) form *3′-chloro-4-nitrodiphenylamine-2-carboxylic acid*, m.p. 272—273° (decomp.), which on ring-closure leads to 5 : 6-, m.p. 201°, and 5 : 8-*dichloro-3-nitroacridine*, m.p. 223°. The 5 : 6-compound with HCl gives *6-chloro-3-nitro-*, m.p. >300°, reduced (Na–Hg) to the *-3-amino-acridine*, m.p. 211—212°. *8-Chloro-3-aminoacridone*, m.p. 267—269°, is obtained by reduction (Na–Hg) of mixed 6- and 8-chloro-3-nitroacridones, followed by fractionation. F. R. S.

Barbituric acids.—See B., 1942, III, 172.

Pyridylquinolines.—See B., 1942, II, 255.

Synthesis of N^1-substituted sulphanilamides. S. Rajagopalan (*Current Sci.*, 1942, **11**, 146).—The following are described: 4-, m.p. 189—190° (lit. 208°), and *ω-sulphanilamidoacetophenone*, m.p. 176—177° (decomp.); *ω-sulphanilamido-α-acetonaphthone*, m.p. 169°; N^4-*acetylsulphanilamidoguanidine*, m.p. 117—118°; 5-, m.p. 243—244° (decomp.), and *7-sulphanilamidoindazole*, m.p. 249—250° (decomp.); 3-N^4′-*acetylsulphanilamido*-1 : 2 : 4-*triazole*, m.p. 204°; 3-*sulphanilamidoindotriazine*, decomp. 200—201°. 3-Aminoindotriazine, m.p. 195—196° (decomp.), is obtained from isatin and aminoguanidine carbonate in AcOH. P. G. M.

Invert soaps. X. Sulphonamidotetrazolium salts: action on the glycolysis of lactic acid bacteria. D. Jerchel (*Ber.*, 1942, **75**, [*B*], 75—81).—CHMe:N·NHPh, diazotised *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$, and cryst. NaOAc in EtOH at 0—10° give N-*phenyl*-N′-p-*sulphonamidophenyl*-C-*methylformazan*, $NHPh{\cdot}N{:}CR{\cdot}N{:}N{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ [(**I**), R = Me], m.p. 235°. Analogously prepared are *compounds* in which R = Pr[a], m.p. 200°, *n*-C_6H_{13}, m.p. 18]°, *n*-C_7H_{15}, m.p. 176°, and *n*-$C_{11}H_{23}$, m.p. 167°. (**I**) is oxidised by $Pb(OAc)_4$ in dry $CHCl_3$ to 2-*phenyl*-3-p-*sulphonamidophenyl*-5-*methyltetrazolium chloride*, $\begin{matrix}N{\cdot}NPh\\ \|\\ CR{-}N\end{matrix}\!\!>\!N^+{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2\}Cl^-$ [(**II**), R = Me], m.p. ~198°. *Compounds*, R = Pr[a], m.p. 179°, *n*-C_6H_{13}, m.p. 147°, *n*-C_7H_{15}, m.p. 142°, and *n*-$C_{11}H_{23}$ (**III**), m.p. 135°, are obtained similarly. Towards *Streptobacterium plantarum* (**III**) is about as active as diphenylundecyltetrazolium chloride or zephirol. H. W.

Bile pigments. XXXI. Intermediate compounds in the transformation of hæmins into bile pigments. E. Stier [with, in part, (Miss) K. Gangl] (*Z. physiol. Chem.*, 1942, **272**, 239—272).—Coproverdohæmin ester is reduced (Pd in 100% HCO_2H at 70—75°) to coproporphyrin I Me_4 ester which is accompanied by coproglaucobilin ester, m.p. 202°. This last substance is also obtained as a by-product of the oxidation of copro-ester-pyridinehæmochromogen, which is transformed by H_2O_2–O_2 into a complex mixture of pigments from which a cryst. material could not be obtained. Oxidation of meso-Me_2 ester-C_5H_5N-hæmochromogen by H_2O_2 and benzoylation of the product leads to *benzoyloxymesoporphyrin Me_2 ester*, m.p. (indef.) 197—199° after softening at 175° (complex *Zn* salt, m.p. 232°). It does not appear to be affected by attempted catalytic hydrogenation but is converted by NaOMe in boiling MeOH–dioxan into hydroxymesoporphyrin Me_2 ester. This with $Fe(OAc)_2$–NaCl at 100° yields hydroxymesohæmin Me_2 ester, converted by C_5H_5N at room temp. into an unseparated mixture of bile pigments. Protohæmin Me_2 ester is transformed by N_2H_4,H_2O in aq. C_5H_5N at 60° into the partly cryst. proto-Me_2 ester–C_5H_5N–hæmochromogen, which is oxidised and benzoylated to *benzoyloxyprotoporphyrin Me_2 ester*, m.p. 219° after softening at 195°. This is catalytically hydrogenated to benzoyloxymesoporphyrin Me_2 ester and converted by NaOMe in MeOH–dioxan into *hydroxyprotoporphyrin Me_2 ester*. Introduction of Fe then leads to hydroxyprotohæmin Me_2 ester, converted into a bile pigment, probably tetramethylhæmatoglaucobilin. Rhodohæmin Me_2 ester and N_2H_4,H_2O in C_5H_5N at 60° afford *rhodo-Me_2 ester-C_5H_5N-hæmochromogen*, m.p. 195° after softening at 182°, whence is obtained *benzoyloxyrhodoporphyrin Me_2 ester*, m.p. 205° after softening at 200°. *Phyllo-ester-C_5H_5N-hæmochromogen* in like manner affords *benzoyloxyphylloporphyrin Me ester*, m.p. (indef.) 224° after softening at 210°, hydrolysed to *hydroxyphylloporphyrin Me ester*. Phylloporphyrin with conc. H_2SO_4 and 20% oleum appears to yield δ-phyllorhodin.

Ætioxanthoporphinogen is transformed by HBr–AcOH at 140—150° into *hydroxyætioporphyrin* (**I**), decomp. 255°. Similarly mesoxanthoporphinogen gives *hydroxymesoporphyrin* (**IX**), m.p. 255—256°, converted by HCl–MeOH into the Me_2 ester, m.p. 171°. H. W.

Reactions of certain thiazoles and glyoxalines with picryl chloride and 2 : 4-dinitrochlorobenzene. J. McLean and G. D. Muir (*J.C.S.*, 1942, 383—386).—Thiazole (improved prep.) and picryl chloride (**I**) give a mixture of *thiazole hydrochloride*, m.p. 139—140°, and *picrylthiazole*, m.p. 172°. 2-Methylthiazole and (**I**) in $COMe_2$ afford *N-picryl-2-methylthiazolium chloride*, m.p. 126° (decomp. in hot EtOH), and a small amount of *picryl-2-methylthiazole*, m.p. 150°. 4-Methylthiazole and (**I**) yield 2-hydroxy-3-picryl-4-methyl-2 : 3-dihydrothiazole (cf. Tomlinson, A., 1937, II, 36). 5-Methylthiazole and (**I**) in $COMe_2$ form the *hydrochloride*, m.p. 81°, and *picryl-5-methylthiazole*, m.p. 111°. 2 : 4-Dimethylthiazole and (**I**) give the *hydrochloride*, m.p. 189°, whilst the 2 : 5-compound affords an $COMe_2$ additive *compound* (?) of picryl-2 : 5-dimethylthiazole, m.p. 172° (decomp.). 1 : 4-Dimethylglyoxaline with (**I**) yields N-*picryl*-1 : 4-*dimethylglyoxalinium chloride*, m.p. 179°, and with 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ forms N-(2 : 4-*dinitrophenyl*)-1 : 4-*dimethylglyoxalinium chloride*, m.p. 227°. N-(2 : 4-*Dinitrophenyl*)-1 : 5-*dimethylglyoxalinium chloride*, m.p. 253°, is similarly obtained. A mechanism for the varying reactions is put forward. F. R. S.

Structural-chemical investigations. VI. Reductive fission of 5-phenyl-4-methylthiazole. H. Erlenmeyer and M. Simon (*Helv. Chim. Acta*, 1942, **25**, 528—530).—$CHPhBr{\cdot}COMe$ and $HCS{\cdot}NH_2$ give *5-phenyl-4-methylthiazole*, b.p. 134—135°/25 mm. (*picrate*, m.p. 147°), reduced by Na and EtOH to $CH_2Ph{\cdot}CHMe{\cdot}NHMe$ (*platinichloride*, m.p. 198—199°; *phenylthiocarbamide* derivative, m.p. 134°). H. W.

Isosteric and structurally similar compounds. XVI. 4-Hydroxybenzthiazole. H. Erlenmeyer and H. Ueberwasser (*Helv. Chim. Acta*, 1942, **25**, 515—521).—*o*-$OMe{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NH_2$ is converted by Br in $CHCl_3$ into *2-amino-4-methoxybenzthiazole*, m.p. 152°, diazotised under strictly defined conditions and then transformed by Gattermann Cu and conc. HCl or HBr into 2-chloro- (**I**), m.p. 66°, or *2-bromo-*, m.p. 71°, *-4-methoxybenzthiazole*. (**I**) with red P and HI (*d* 1·7) in boiling AcOH gives 4-hydroxybenzthiazole, converted by oleum at the temp. of ice and salt into *4-hydroxybenzthiazole-5 : 7-disulphonic acid*, and by conc. H_2SO_4 at room temp. into the *-7-sulphonic acid*, which with I–KI in neutral solution gives *5-iodo-4-hydroxybenzthiazole-7-sulphonic acid* (*K* salt). *5-Chloro-2-methoxyphenylthiocarbamide*, m.p. 144—145° (NN′-5 : 5′-*dichloro*-2 : 2′-*dimethoxydiphenylthiocarbamide*, m.p. 165—166°), similarly affords *7-chloro-2-amino-4-methoxybenzthiazole*, m.p. 203°, diazotised and converted into 2 : 7-*dichloro-*, m.p. 124°, and *7-chloro-2-bromo-*, m.p. 141—142°, *-4-methoxybenzthiazole*. Partial dehalogenation of these compounds to *7-chloro-4-methoxybenzthiazole* (**II**), m.p. 92—94°, succeeds if the Raney Ni catalyst is kept saturated with H_2. *7-Chloro-4-methoxy-2-ethoxybenzthiazole* has m.p. 87—88°. (**II**) is dealkylated by 48% HBr at 170—180° to *7-chloro-4-hydroxy-*, m.p. 211° after partial sublimation, converted by I–KI in neutral solution into *7-chloro-5-iodo-4-hydroxy-*, m.p. ~195° (decomp.), *-benzthiazole*. H. W.

Highly *C*-alkylated 2-amino-1 : 3 : 4-thiodiazoles and their sulphanilamide derivatives. H. Arnold (*Ber.*, 1942, **75**, [*B*], 87—93).—Hydnocarpyl chloride and $NH_2{\cdot}CS{\cdot}NH{\cdot}NH_2$ (**I**) at 60—70° give *5-amino-2-norhydnocarpyl*-1 : 3 : 4-*thiodiazole*, m.p. 150—152° (*hydrochloride*, m.p. 112—114°), converted by *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ in dry C_5H_5N at 60° into *5-p-acetamidobenzenesulphonamido-2-norhydnocarpylthiodiazole*, m.p. 117—119°, which is hydrolysed to the 5-p-NH_2-compound, m.p. 117—118° (softens at 113°). Oleyl chloride and (**I**) at 110° yield *5-amino-2-α-Δ^9-heptadecenyl*-1 : 3 : 4-*thiodiazole*, m.p. 150—160° (softens at 110°) (*hydrochloride*, m.p. 85—90°), which yields *5-p-acetamidobenzenesulphonamido-2-α-Δ^9-heptadecenyl*-1 : 3 : 4-*thiodiazole*, m.p. 104—106°, and the Ac-free *compound*, m.p. 109—111°. Analogously, $CHPh{:}CH{\cdot}COCl$ affords *5-amino-*, m.p. 233—235° (*hydrochloride*, m.p. 230—232°), *5-p-acetamidobenzenesulphonamido-*, m.p. 202—204°, and *5-p-aminobenzenesulphonamido-*, m.p. 285—286°, *-2-styryl*-1 : 3 : 4-*thiodiazole*. H. W.

VII.—ALKALOIDS.

***Strychnos* alkaloids. CXIV. Condensations of dihydro-ψ-strychnine and -brucine with acetic anhydride, malonic acid, and hydrocyanic acid.** H. Leuchs and K. D. Gundermann (*Ber.*, 1942, **75**, [*B*], 168—173).—Dihydro-ψ-strychnine (**I**) is converted by Ac_2O at 100° into *dihydrostrychnine-9-acetic acid* (**II**), m.p. 300—303° (vac.; decomp.), $[\alpha]_D^{20}$ +43·0° in H_2O [*Na* salt; *Me* ester, m.p. 227—228° (vac.; decomp.), and its *methiodide*], converted by Br–HBr into bromodihydrostrychnine-9-acetic acid, m.p. 290° (vac.). (**II**) is also obtained from (**I**) and $CH_2(CO_2H)_2$. (**I**) and KCN in AcOH afford *dihydrostrychnine-9-nitrile*, m.p. 283—286° (vac.; slight decomp.) (*hydrochloride*; *perchlorate*).

[With Y. Hwang.] Dihydro-ψ-brucine (**III**) is converted by Ac_2O and NaOAc at 100° into *dihydrobrucine-9-acetic acid* (**IV**), m.p. 282—284° (vac.; decomp.), $[\alpha]_D^{20}$ +33·1°/*d* in AcOH (*perchlorate*, decomp. 260—280°), and *N-acetyl*-sec.-ψ-*dihydrobrucine*, apparently two forms, m.p. 80—90°, becoming resinous at 155—185°, and m.p. ~160° (decomp.); with Ac_2O–C_5H_5N at 100° (**IV**) does not appear to be produced. (**IV**) does not react with NH_2OH in AcOH at 100°, and is not catalytically hydrogenated in HCl or AcOH. It gives a non-cryst. *Et* ester (*picrate*, m.p. 120—140°), and *Me* ester, m.p. 200° (vac.) [*picrate*, m.p. 231—235° (decomp.) after softening at 210°; *methiodide*, m.p. 190° decomp. ~218°]. (**IV**) is oxidised by 2N-HNO_3 at 0° to the quinone, $C_{23}H_{24}O_6N_2$ (*perchlorate*), reduced by SO_2 to the corresponding quinol (*perchlorate*). With CrO_3–dil. H_2SO_4 at 70—80° (**IV**) gives a *substance*, $C_{19}H_{24}O_7N_2$, m.p. 230—232° (vac.; decomp.) (softens at 220°). (**IV**), PhCHO, and NaOMe in boiling MeOH afford *benzylidenedihydrobrucine-9-acetic acid* [*perchlorate*, m.p. 245—255° (decomp.) (darkens at 180°)]. (**IV**) is also produced from (**III**) and $CH_2(CO_2H)_2$. With KCN in AcOH (**III**) yields *dihydrobrucine-9-nitrile*, m.p. 176—178° (vac.; decomp.) (*hydrochloride*; *perchlorate*). H. W.

Alkaloids from Koto-tzuzarafuji (*Stephania sasakii*, **Hayata**).—See B., 1942, III, 172.

Alkaloids of *Lycopodium* species. I. *L. complanatum*, L. R. H. F. Manske and L. Marion (*Canad. J. Res.*, 1942, **20, B**, 87—92).—From *L. complanatum*, L., the following alkaloids are obtained: lycopodine, $C_{16}H_{25}ON$ [*perchlorate*, m.p. 283° (decomp.)], nicotine (its first recorded occurrence in a pteridophyte), and the new compounds, *complanatine* (LI), $C_{18}H_{31}ON$, m.p. 169° (*perchlorate*, $+H_2O$, m.p. 194°), and *alkaloids* L2, $C_{18}H_{29}O_2N$, m.p. 97° (*perchlorate*, m.p. 231°), L3, $C_{18}H_{31}O_2N$ (*perchlorate*, m.p. 246°), L4, $C_{16}H_{27}N$ (*perchlorate*, $+0{\cdot}5H_2O$, m.p. 225°), L5, $C_{18}H_{28}O_2N_2$ (*perchlorate*, m.p. 282°), and *obscurine*, L6, $C_{18}H_{28}ON_2$ (*diperchlorate*, $+H_2O$, m.p. 299°, with some previous decomp.). Nicotine is also isolated from *Equisetum arvense*, L. Hydrolysis (dil. H_2SO_4) of the H_2O-insol. polysaccharides from (**I**) gives *d*-galactose. A. T. P.

VIII.—ORGANO-METALLIC COMPOUNDS.

Veratral-6-arsinic acid. A. A. Schamschurin (*J. Gen. Chem. Russ.*, 1941, **11**, 647—649).—6-Nitroveratrole on reduction with $FeSO_4$–aq. NH_3 gives 87% of 6-aminoveratrole, which by the Bart reaction affords 46% of 4 : 5-*dimethoxybenzaldehyde-6-arsinic acid*, m.p. ~300° (decomp.) (semicarbazone, m.p. 256°). The acid is stable to boiling 15% HCl and is oxidised by $KMnO_4$ to 4 : 5-*dimethoxy-2-carboxyphenylarsinic acid*, m.p. 300° (retains 1 H_2O at 100°). G. A. R. K.

Organic compounds of mercury. V. Interaction of mercury dialkyls with mercury salts of tribasic acids. N. N. Melnikov and M. S. Rokitzkaja (*J. Gen. Chem. Russ.*, 1941, **11**, 592—595).—Hg dialkyls do not react with Hg salts in org. solvents (cf. A., 1938, II, 166), but in presence of small amounts of H_2O good yields of alkyl Hg salts are obtained. The following have been prepared (% yield in parentheses): $(HgMe)_3PO_4$, decomp. 182° (80), $(HgEt)_3PO_4$, m.p. 179—180°, monohydrate, m.p. ~110° (98), $(HgEt)_3AsO_4$, m.p. 184—186° (75), HgEt·NO_3, m.p. 86—86·5° (80—85), $(HgPr^{\alpha})_3PO_4$, m.p. 96° (98), $(HgBu^{\alpha})_3PO_4$, m.p. 75° (88), $(HgC_5H_{11}\text{-}iso)_3PO_4$, m.p. 105° (62). G. A. R. K.

Electric moments of organomercuric halides in dioxan.—See A., 1942, I, 293.

IX.—PROTEINS.

Oxazoline and thiazoline rings in proteins. S. Blackburn, W. R. Middlebrook, and H. Phillips (*Nature*, 1942, **150**, 57).—Activated peptide linkings which undergo methylation may be those which have undergone condensation with the side-chains of β-OH-acids giving rise to oxazoline rings. Free cysteine side-chains in reduced wool may form thiazoline rings. A. A. E.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Behaviour of some lignin preparations in the molecular still. J. F. Hechtman (*Paper Trade J.*, 1942, **114**, *TAPPI Sect.*, 259—264).—A pot still has been constructed so that the reservoir and condensing surfaces are removable for weighing. The distillation characteristics of native lignin (**I**), CH_2N_2-methylated lignin (**II**), fully methylated lignin (**III**), and Willstätter lignin (**IV**), all from black spruce, were examined. At 260°/1 μ. pressure, (**I**) gave 4% of distillate; both residue and condensate had the same OMe content as the original. Ultra-violet absorption curves and solubility characteristics indicated that the residue might be of higher and the condensate of lower mol. wt. than (**I**). At >290°/>1 μ. decomp. occurred. At 290°/1 μ. (**II**) gave 6% of condensate containing 17·7% OMe; the OMe content of the residue was 20·9% and of the original 21·1%. Even at 350°/1 μ. no distillate was obtained from (**III**), although non-condensable material was lost. Under the same conditions (**IV**) too yielded no condensate, and only 2% of volatile material was lost after 20 hr. At 260°/25—50 μ. (**IV**) gave a considerable condensate (OMe content 14·0%), but when air was replaced by N_2 no condensate was obtained even at 350°. The significance of these results is discussed. H. A. H.

XI.—ANALYSIS.

Micro-Kjeldahl nitrogen determination without use of titration procedure. W. H. Taylor and G. F. Smith (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 437—439).—The Wagner micro-Kjeldahl procedure is modified by absorption of the NH_3 in aq. H_3BO_3, dilution to a standard vol., and electrometric titration to a definite p_H, the results being interpreted by a preformed calibration curve. J. D. R.

Micro-determination of sulphur and halogens.—See A., 1942, I, 276.

Potentiometric titration of dibasic acids.—See A., 1942, I, 306.

Colorimetric estimation of arginine and histidine. H. T. Macpherson (*Biochem. J.*, 1942, **36**, 59—63).—Arginine is determined by a modification of Weber's method (A., 1930, 755) in which the $CO(NH_2)_2$ is added prior to the OBr′ and the colour developed in two stages [*i.e.*, by repetition of the addition of $CO(NH_2)_2$ and OBr′] to ensure max. and consistent colour development. Since the colour does not obey Beer's law a photometer is preferable to a colorimeter and 0·02±0·001 mg. may be determined. Histidine is determined by a modification of the method of Jorpes (A., 1932, 1270) in which the reaction with sulphanilic acid and $NaNO_2$ is carried out at room temp., Na_2CO_3 used for colour development, and the colour stabilised by slightly alkaline EtOH. The final colour may be measured in a colorimeter since it obeys Beer's law. H. G. R.

Determination of terpinyl acetate and other esters. H. M. Perry and T. F. West (*Analyst*, 1942, **67**, 159—161).—The B.P. 1932 method for the determination of esters with 0·5N-KOH–EtOH gives low results with terpinyl acetate, some other terpinyl esters, and menthyl valerate. Boiling ~1·5 g. of the sample with 40 ml. of 0·5N-KOH in OH·$[CH_2]_2$·OEt for 30 min. completely saponified all the 30 esters tested except terpinyl propionate, which required 40 min. The reagent is suitable for determining terpenic alcohols after acetylation or formylation. Data are given for a no. of esters, alcohols, and essential oils. T. F. W.

Determination of quercetin-like substances using a Klett-Summerson photoelectric colorimeter. C. W. Wilson, L. S. Weatherby and W. Z. Bock (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 425—426).—The sample is mixed with a solution of citric and boric acids in anhyd. $COMe_2$ and the colour produced measured in a Klett-Summerson photoelectric colorimeter. Recovery of added quercetin was quant. J. D. R.

Gravimetric determination of flavines. B. A. Ellis (*Analyst*, 1942, **67**, 226—227).—Euflavine and acriflavine are determined directly by pptn. from aq. solution as the picrate, $C_{20}H_{17}O_7N_6$ (**I**). A certain excess of picric acid is necessary and (**I**) is washed with ice-cold H_2O, dried at 100°, and weighed. The filtrate may be used for determination of Cl′, due allowance being made for the Cl derived from the euflavine. Shell dressings are extracted with acidified EtOH, and after adding H_2O the extract is evaporated to low bulk, filtered, and (**I**) pptd. as above. Sterilisation of the dressings reduced the recoveries of flavines. S. B.

Colorimetric (*p*-dimethylaminobenzaldehyde–sulphuric acid) method for determining small quantities of atropine. R. P. Daroga (*J. Indian Chem. Soc.*, 1941, **18**, 579—584).—Conditions for the max. sensitivity of a colorimetric method for atropine (**I**) have been worked out. The test solution is treated with 0·1 c.c. of reagent (made as required by diluting a 20% solution of *p*-NMe_2·C_6H_4·CHO in conc. H_2SO_4 with H_2O, 1 : 1) and warmed for 30 min. (steam-bath). After diluting to 25 c.c. the violet colour is matched against permanent standards in a tintometer. A linear relationship between concn. of (**I**) and colour intensity is shown to exist. W. C. J. R.

Determination of cystine content of proteins by means of sulphuric, hydrochloric, hydriodic, and mixtures of hydrochloric and formic acids. W. C. Hess and M. X. Sullivan (*J. Washington Acad. Sci.*, 1942, **32**, 130—132).—Similar vals. are obtained for cystine in a variety of proteins whatever hydrolysing agent is used, except that HI gives slightly higher vals. owing to non-formation of humin. P. G. M.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

OCTOBER, 1942.

I.—ALIPHATIC.

Classical methods in the analysis of the fine structure of carbon compounds. A. Lüttringhaus (*Naturwiss.*, 1942, **30**, 40—45). H. W.

Preparation and reactions of free methyl at low temperatures. G. Semerano and L. Riccoboni (*Z. physikal. Chem.*, 1941, **189**, **A**, 203—218).—At −40° AgMe decomposes yielding free Me which is rapidly converted into C_2H_6. The properties of Me are discussed. C. R. H.

Allylic rearrangements. XII. Action of dioxan on magnesium butenyl bromide. W. G. Young and H. H. Pokras (*J. Org. Chem.*, 1942, **7**, 233—240).—Addition of dioxan to Mg butenyl bromide (**I**) in Et_2O produces a solution of Mg dibutenyl (**II**) and a ppt. containing a (**I**)–dioxan complex (**III**). Hydrolysis of (**II**) gives 44·5% of CH_2:CHEt (**IV**), 32·2% of *cis*-CHMe:CHMe (**V**), and 23·2% of *trans*-CHMe:CHMe (**VI**) and hydrolysis of (**III**) yields 55% of (**IV**), 28% of (**V**), and 17% of (**VI**). An allylic rearrangement is considered to occur during the formation of (**II**). H. W.

Catalytic dimerisation of *iso*butene by activated copper sulphide. A. Wassermann and W. T. Weller (*Nature*, 1942, **149**, 669).—The main product is a mixture of the two ββδ-trimethylpentenes. A. A. E.

[Preparation of] conjugated diolefines by displacement of ethylenic linkings. A. L. Henne and A. Turk (*J. Amer. Chem. Soc.*, 1942, **64**, 826—828).—When passed over activated Al_2O_3 at 365°, $(CH_2{\cdot}CH{:}CH_2)_2$ gives $(CH{:}CHMe)_2$ (39%), b.p. 82·0°, and $CH_2{:}CH{\cdot}CH{:}CHEt$ (3%), b.p. 72·9°; $(CH_2{:}CMe{\cdot}CH_2)_2$ gives $(CH{:}CMe_2)_2$ (81%), f.p. 13·94°, b.p. 134·5°; $CH_2{:}CMe{\cdot}[CH_2]_2{\cdot}CH{:}CH_2$ gives $CMe_2{:}CH{\cdot}CH{:}CHMe$ (58%), m.p. −74·6°, b.p. 111·5°; $CH_2{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}CH_2$ gives (?) $CH_2{:}CH{\cdot}CH{:}CMeEt$ (14%), b.p. 111°; $CH_2{:}CH{\cdot}[CH_2]_2{\cdot}CH{:}CHMe$ gives $CH_2{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}CH_2$ (8%) and, by rearrangement, $CHMe{:}CH{\cdot}CH{:}CHEt$ (6%), b.p. 109·6°; $CH_2{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}CHMe$ gives $CHMe{:}CH{\cdot}CH{:}CMeEt$ (4%), b.p. 135·2°; $(CH_2{\cdot}CH{:}CHMe)_2$ gives $(CH{:}CHEt)_2$ (0·5%). Rearrangement to conjugated dienes is easiest when the ethylenic linking moves towards the centre of the chain and is further facilitated by presence of Me on one of the C of this linking. $(CH{:}CHR)_2$ give cryst., but $(CH{:}CR_2)_2$ or $CHR{:}CH{\cdot}CH{:}CR_2$ give polymeric, adducts with $(:CH{\cdot}CO)_2O$. 3-*Ethyl*-, m.p. 52°, 3 : 4 : 6-*trimethyl*-, m.p. 76°, and 3-*methyl*-6-*ethyl*-, m.p. 70·5°, -1 : 2 : 3 : 6-*tetrahydrophthalic anhydride* are described. R. S. C.

Macromolecular compounds. CCXCII. Poly*iso*butylene. H. Staudinger, G. Berger, and K. Fischer (*J. pr. Chem.*, 1942, [ii], **160**, 95—119).—Properties of poly*iso*butylene of varying degrees of polymerisation are recorded, and the relationship between η and polymerisation is examined. A. T. P.

Isolation of δ-methyl-$\Delta^{\alpha\gamma}$-pentadiene. G. B. Bachman and C. G. Goebel (*J. Amer. Chem. Soc.*, 1942, **64**, 787—790).—$CMe_2{:}CH{\cdot}CH{:}CH_2$ (**I**) and $CH_2{:}CMe{\cdot}CH{:}CHMe$ (**II**), obtained by dehydration of $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}CHMe{\cdot}OH$, are separated by heating with $(:CH{\cdot}CO)_2O$ (**III**) alone or in PhMe or dioxan. (**II**) yields 3 : 5-dimethyl-Δ^4-tetrahydrophthalic anhydride. (**I**) is unchanged or forms a linear co-polymeride (**IV**) (reaction inhibited by quinol and accelerated by Bz_2O_2) and is thus obtained in 23% yield, having b.p. 76·3°. Oxidation of (**IV**) to a substance having the same η, *i.e.*, absence of ring-fission, indicates the structure shown, the mol. wt. varying from 8700 to 103,000. Preliminary data are recorded for hetero-polymerisation of (**I**), (**III**), and other unsaturated compounds. R. S. C.

$$\left[\cdot CH\text{—}CH\text{—}CH\text{—}CH_2\cdot\right]_x \quad \begin{matrix} & & & \\ CO{\cdot}O{\cdot}CO & & CH{:}CMe_2 & \end{matrix}$$
(**IV.**)

Prolycopene. A. L. LeRosen and L. Zechmeister (*J. Amer. Chem. Soc.*, 1942, **64**, 1075—1079).—The pigments of ripe fruits of *Lycopersicum esculentum* (tangerine tomato) are separated by adsorption on $Ca(OH)_2$ into *prolycopene* (**I**), $C_{40}H_{56}$, m.p. 111° (corr.; block) (main constituent; 18·7 mg. per kg. of fruit) (cf. A., 1942, II, 126), lycopene (**II**), and neolycopene-*A*. The absorption (max. at 470 and 443·5 mμ. in light petroleum; given also for 10 other solvents) indicates that 5—7 of the ethylenic linkings of (**I**) are *cis* and the remainder *trans*. (**I**) absorbs O_2 very readily in air but is stable in solution, *e.g.*, in boiling light petroleum. When melted in CO_2 it gives ~12 layers on chromatography, due mainly to stereoisomerides of (**II**) and including pigments having absorption max. at 464 and 438 mμ. With I in light petroleum it gives very rapidly a complex mixture including much (**II**). R. S. C.

New method of β-chloroethylation. L. Bert (*Compt. rend.*, 1941, **213**, 1015—1016).—Cl·$[CH_2]_2$ derivatives are prepared from *Cl*·$[CH_2]_2$ *benzenesulphonate* (from $PhSO_2Cl$ and Cl·$[CH_2]_2$·OH), b.p. 192°/15 mm., and RMgX in Et_2O. A. Li.

Dielectric behaviour, supercooling, and vitrification of chlorobutanes and chloropentanes.—See A., 1942, **I**, 289.

Synthesis of aliphatic difluorides. (Miss) M. W. Renoll (*J. Amer. Chem. Soc.*, 1942, **64**, 1115—1116).—$CH_2{:}CRCl$ or $CHR{:}CRCl$, when mixed with HF at −78° and warmed slowly to 35—46° with occasional release of HCl (4—11 atm.), gives 59—70% of $CRR'F_2$ with a little $CRR'ClF$ and >25% of $CRR'Cl_2$. $CHR{:}CRCl$ is the main product when $COR{:}CH_2R$ reacts with PCl_5 at 20—30°. Thus, in HF $CH_2{:}CPr^{\alpha}Cl$ gives $CMePr^{\alpha}F_2$ (64·1%), f.p. −98·1°, b.p. 60·1°, and $CMeEtCl_2$ (13·9%). $CH_2{:}CEtCl$ or $CHMe{:}CMeCl$ gives 67% of $CMeEtF_2$, f.p. −114·0°, b.p. 31·0°. $CHMe{:}CEtCl$ gives *γγ-difluoro-n-pentane* (59·7%), f.p. −94·0°, b.p. 60·8°. $CH_2{:}CBu^{\beta}Cl$ gives *ββ-difluoroisohexane* (70·5%), f.p. −112·7°, b.p. 78·2°. n-C_5H_{11}·$CH{:}CMeCl$ gives *ββ-difluoro-n-octane* (58·9%), f.p. −50·0°, b.p. 136·3—136·6°/760 mm. (slight decomp.), 66·2—66·6°/60 mm. R. S. C.

Preparation and directed chlorination of *aaa*-trifluoropropane. A. L. Henne and A. M. Whaley (*J. Amer. Chem. Soc.*, 1942, **64**, 1157—1159).—$CHMeCl{\cdot}CHCl_2$ [prep. from $CHMeCl{\cdot}CH_2Cl$ by Cl_2 and Fe filings at the b.p. (dark)], b.p. 130—133°, with 20% aq. KOH gives $CHMe{:}CCl_2$ (90%), b.p. 75—77°, which with HF at 75° and later 95° (intermittent removal of HCl; 20 atm.) and then with SbF_3–Cl_2 at 13 atm. (free flame) gives *aaa-trifluoropropane* (**I**) (36%), f.p. −148·8°, b.p. −13°, and *α-chloro-aa-difluoropropane* (**II**) (36%), b.p. 25·8° [as above yields (**I**)]. With HCl–$AlCl_3$ (2—3%), $CHMe{:}CCl_2$ gives $CEtCl_3$ (45%), which with SbF_3 loses much HCl, giving 5—10% of (**I**) and 10% of (**II**) + $CEtCl_2F$, b.p. 66·6°. No exchange of halogen occurs with $CH_2{:}CH{\cdot}CCl_3$ and SbF_3. With Cl_2–H_2O in light, (**I**) gives, successively, γ-chloro- (**III**), f.p. −106·2°, b.p. 45·1°, *γγ-dichloro-* (**IV**), f.p. −93·2°, b.p. 72·4°, *γγγ-trichloro-* (**V**), f.p. −41·7°, b.p. 95·1°, and *ββγγγ-pentachloro-* (**VI**), f.p. −109·0°, b.p. 153·1°, *-aaa-trifluoropropane*. Under similar conditions $CEtCl_3$ gives $CHMeCl{\cdot}CCl_3$ (15—20%), $Cl{\cdot}[CH_2]_2{\cdot}CCl_3$ (5—10%), $CMeCl_2{\cdot}CCl_3$ (30%), $CH_2Cl{\cdot}CHCl{\cdot}CCl_3$ (10—15%), and $CHCl_2{\cdot}CH_2{\cdot}CCl_3$ (5%). $CHMeCl{\cdot}CCl_3$ with HF and HgO at 100° give *β-chloro-aaa-trifluoropropane* (80%), b.p. 30°, and thence *ββ-*, f.p. 13·8°, b.p. 48·8°, + *βγ-dichloro-aaa-trifluoropropane*, b.p. 76·7°, and (**VI**). With alcoholic alkali, (**IV**) gives $CHCl{:}CH{\cdot}CF_3$, which with Cl_2 gives $CHCl_2{\cdot}CHCl{\cdot}CF_3$, b.p. 106·8°. (**III**) does not react with Mg or MgEtBr and with KOH loses HCl. (**IV**) and alcoholic alkali give $CHCl{:}CH{\cdot}CF_3$ (100%). (**V**) loses HCl to alkali, and with HgF_2 gives $CH_2(CF_3)_2$. With $SbCl_2F_3$, (**VI**) gives *ββγγ-tetrachloro-aaaγ-tetrafluoro-*, f.p. 41·74° b.p. 112·4°, and *ββγ-trichloro-aaaγγ-pentafluoro-propane*, f.p. −4·3°, b.p. 72·0°. $CHMe{:}CClF$, b.p. 24·8°, *aaβ-tri-*, f.p. −114·7°, b.p. 88·3°, *aβ-*, f.p. −109·2°, b.p. 53·7°, and *aa-di-chloro-γγγ-trifluoropropylene*, f.p. −87·2°, b.p. 55·1°, are also described. R. S. C.

Manufacture of organic nitro-compounds.—See B., 1942, II, 249.

Number of stereoisomeric alcohols. E. S. Allen and H. Diehl (*Iowa State Coll. J. Sci.*, 1942, **16**, 161—167).—A method is given for computing the no. of stereoisomeric monosubstituted saturated hydrocarbons having a given no. of C atoms, by considering the groups attached to the substituted C atom. A. Li.

Action of hydrogen fluoride, sulphuric acid, and phosphoric acid on optically active butan-β-ol. R. L. Burwell, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 1025—1031).—Optically active butan-β-ol (**I**) is racemised {first order with respect to (**I**) and decreases with $[H_2O]$} by H_2SO_4 under less drastic conditions than those which promote alkylation, polymerisation, or butylene evolution. The activation energy is ~22,000 g.-cal. and, on the carbonium ion hypothesis, the racemisation has been correlated with other reactions between H_2SO_4 and (**I**). Similar reactions occur with HF but much larger ratios of acid to alcohol are required. Only slight racemisation occurs with H_3PO_4.

Order of addition of hydrogen halides to halogenated α-oxides. A. A. Petrov (*J. Gen. Chem. Russ.*, 1941, **11**, 713—721).—α- and α′-Methylepichlorohydrins and the corresponding bromohydrins undergo ring fission with H halides, giving rise to alcohols $CHMeHal{\cdot}CH(OH){\cdot}CH_2Hal$. Crotyl bromide, b.p. 104·5—106·5°, is hydrolysed to a mixture of $OH{\cdot}CHMe{\cdot}CH{:}CH_2$, b.p. 95—97°, and $CHMe{:}CH{\cdot}CH_2{\cdot}OH$, b.p. 121—122°, separated by fractionation. Addition of Br in $CHCl_3$ affords, respectively, *γδ-dibromobutan-β-ol*, b.p. 94·5°/10 mm. (*acetate*, b.p. 108—108·5°/10 mm.), and *βγ-dibromobutan-α-ol*, b.p. 99·5°/10 mm. (*acetate*, b.p. 109·5°/10 mm.). With aq. KOH these yield *α-methyl-α′-bromomethylethylene oxide* (**I**) (70%), b.p. 144—145·5°, 54·5—55°/25 mm., and *α-bromoethylethylene oxide* (50%), evidently a mixture of two stereoisomerides, the main fraction (**II**), b.p. 142—148°, and (**III**), b.p. 152—154°; these are accompanied by (?) divinyl oxide, b.p. 62—68°. (**II**) with fuming HCl yields *α-chloro-γ-bromobutan-β-ol* (**IV**), b.p. 76—76·5°/10 mm. (*acetate*, b.p. 92·5—93°/10 mm.), oxidised to α-chloro-γ-bromobutanone, b.p. 67—68°/10 mm. (**II**) with HBr gives *αγ-dibromobutan-β-ol* (**V**), b.p. 90·5—91°/10 mm. (*acetate*, b.p. 105—106°/10 mm.); (**III**) gives an isomeride, b.p. 90·5—91°/10 mm.; both are oxidised to the same *αγ-dibromobutanone*, b.p. 76·5—77°/10 mm.; with KOH both give the same oxide (**I**). (**I**) with HCl affords *γ-chloro-α-bromobutan-β-ol* (**VI**), b.p. 76·5—77°/10 mm. (*acetate*, b.p. 94·5—95·5°/10 mm.), oxidised to *γ-chloro-α-bromobutanone*, b.p. 64·5—65°/10 mm. (**I**) with HBr gives (**V**). (**IV**) with KOH gives *α-methyl-α′-chloromethylethylene oxide* (**VII**), b.p. 124—125·5°; (**VI**) similarly gives *α-chloroethylethylene oxide* (**VIII**), b.p. 118—124°, and a smaller amount of an *isomeride*, b.p. 133—135°. (**VIII**) with HCl gives *αγ-dichlorobutan-β-ol* (**IX**), b.p. 63—64°/10 mm. (*acetate*, b.p. 82·5—83·5°/10 mm.); the higher-boiling isomeride of (**VIII**) gives a product, b.p. 63—64°/10 mm.; both are oxidised to αγ-dichlorobutan-β-one, b.p. 55—55·5°/10 mm. (**VIII**) with HBr gives (**VI**). (**VII**) with HCl gives (**IX**) and with HBr, (**IV**). All the halogenated ketones are reduced with Zn and AcOH to COMeEt.

G. A. R. K.

Migratory ability of acetylenio radicals in transposition reactions. Study of the heptinene radical in the dehalogenation by magnesium of the chlorohydrin $C_5H_{11}{\cdot}C{:}C{\cdot}CR(OH){\cdot}CH_2Cl$. M. Tiffeneau and Y. Deux (*Compt. rend.*, 1941, **213**, 753—758).—Mg heptinyl bromide (**I**) (obtained from MgEtBr and heptinene) with $COMe{\cdot}CH_2Cl$ affords *α-chloro-β-methyl-Δ$^{\gamma}$-noninen-β-ol*, giving at 110° Δ$^{\delta}$-decinen-β-one (**II**), b.p. 94—95°/20 mm. (semicarbazone, m.p. 128°), not identical with Δ$^{\delta}$-decinen-γ-one (semicarbazone, m.p. 108—109°), from EtCOCl and Na compound of heptinene. Hydrogenation of (**II**) (Raney Ni) yields decan-β-one (semicarbazone, m.p. 120°) identical with that afforded by decan-β-ol (from Mg octyl bromide and MeCHO) and CrO_3. (**I**) and α-chlorobutan-β-one afford *α-chloro-β-ethyl-Δ$^{\gamma}$-noninen-β-ol*, giving at 110° Δ$^{\epsilon}$-undecinen-δ-one, b.p. 100—101°/20 mm. (semicarbazone, m.p. 143—144°), identical with that from Pr$^{\alpha}$COCl and the Na derivative of heptinene. (**I**) and $COPh{\cdot}CH_2Cl$ yield *α-chloro-β-phenyl-Δ$^{\gamma}$-noninen-β-ol*, which at 110° gives α-phenyl-Δ$^{\gamma}$-noninen-β-one, b.p. 170°/18 mm. (semicarbazone, m.p. 84—85°), identical with that from $CH_2Ph{\cdot}COCl$ and the Na derivative of heptinene. Migratory ability is Ph, Et > heptinenyl > Me. The heptinenyl radical is of the "aliphatic" type, but $CH{:}C$ (work in progress) may be of the "aromatic" type (cf. vinyl) and C_5H_{11}-substitution may have a weakening effect. Me migrates in *βδεη*-tetramethyl-Δ$^{\beta\zeta}$-octadiene-δε-diol to yield *ββδη*-tetramethyl-Δ$^{\delta\zeta}$-octadien-ε-one. Thus, substitution in vinyl to give *iso*butenyl has made its migratory power weaker than Me.

C. S.

Utilisation of aliphatic nitro-compounds. III. Nitro-alcohols prepared from aldehydes containing no other functional groups. C. A. Sprang with E. F. Degering (*J. Amer. Chem. Soc.*, 1942, **64**, 1063—1064; cf. A., 1940, II, 3).—$CH_2R{\cdot}NO_2$ and R′CHO are condensed by alkali to give $NO_2{\cdot}CHR{\cdot}CHR'{\cdot}OH$, the best conditions depending on the nature of R and R′. Thus are obtained *α-nitro*-n-*nonan-β-ol*, b.p. 120—121°/1 mm., -n-octan-β-ol, b.p. 120°/2 mm., and -n-*hendecan-β-ol*, b.p. 140°/2 mm., *β-nitro*-n-*nonan-γ-ol*, b.p. 110°/1·5 mm., -n-*decan-γ-ol*, b.p. 125°/2 mm., -n-*hendecan-γ-ol*, b.p. 128°/1·8 mm., -n-*tridecan-γ-ol*, b.p. 153—155°/2 mm., *-β-methyl*-n-*nonan-γ-ol*, b.p. 109°/1 mm., *-β-methyl*-n-*decan-γ-ol*, b.p. 124—125°/1·2 mm., and *-β-methyl*-n-*hendecan-γ-ol*, b.p. 125°/3 mm., *γ-nitro*-n-*hendecan-δ-ol*, b.p. 128°/2 mm., -n-*dodecan-δ-ol*, b.p. 138—140°/2·2 mm., -n-*tetradecan-δ-ol*, b.p. 150—155°/1·5 mm., *-γ-methyl*-n-*hexan-β-ol*, b.p. 97°/5 mm., *-γ-methyl*-n-*nonan-δ-ol*, b.p. 99—101°/1·5 mm., *-γ-methyl*-n-*octan-δ-ol*, b.p. 90—94°/2·5 mm., *-γ-methyl*-n-*decan-δ-ol*, b.p. 128°/1·3 mm., and *-γ-methyl*-n-*hendecan-δ-ol*, b.p. 111°/1·5 mm., and *δ-nitro*-n-*hendecan-ε-ol*, b.p. 135°/2 mm., and -n-*dodecan-ε-ol*, b.p. 130°/1·2 mm. *n* and *d* are given.

R. S. C.

Synthesis of *dl*-octane-αβ-diol and its homologues. C. Niemann and C. D. Wagner (*J. Org. Chem.*, 1942, **7**, 227—232).—Addition of $OEt{\cdot}CHBr{\cdot}CH_2Br$ to *n*-$C_{11}H_{23}{\cdot}MgBr$ in Et_2O affords *n*-octacosane, m.p. 61·5°, and Et β-bromo-α-tetradecyl ether, b.p. 145—165°/2 mm., m.p. 23·5°, transformed by Zn dust in boiling Bu$^{\alpha}$OH into Δ$^{\alpha}$-hexadecene (**I**), b.p. 122·0—122·5°/3 mm., m.p. 4°, and tetradecanol. (**I**) is converted by AgOBz and I in boiling C_6H_6 followed [illegible] radecane-αβ-diol, m.p. 73·1—73·6° (*CMe$_2$ ether*, m.p. 22·9°; *diacetate*, m.p. 30°; *di*-N-*phenylcarbamate*, m.p. 95°). Similarly, *n*-$C_{16}H_{33}Br$ gives Et β-bromo-α-hexadecyl ether, m.p. 28·5—29·5° (with dotriacontane, m.p. 69·0°), and thence Δ$^{\alpha}$-octodecene, b.p. 144—146°/3 mm., m.p. 17·5, and *octadecane-αβ-diol*, m.p. 79·0—79·5° (*CMe$_2$ ether*, m.p. 31·3°; *diacetate*, m.p. 40°; *di*-N-*phenylcarbamate*, m.p. 99·5°). Analogously, *n*-$C_{18}H_{37}Br$ gives successively Et β-bromo-α-octadecyl ether, which could not be distilled without decomp., Δ$^{\alpha}$-eicosene, b.p. 151°/1·5 mm., m.p. 28·5°, and *eicosane-αβ-diol*, m.p. 84·3—84·8° (*CMe$_2$ ether*, m.p. 36·7°; *diacetate*, m.p. 47°; *di*-N-*phenylcarbamate*, m.p. 103·5°).

H. W.

Structure of αγδζ-dimethylenedulcitol. R. M. Hann, W. T. Haskins, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 986—987).—The structure of αγδζ-dimethylenedulcitol (prep. from dulcitol by warm 37% CH_2O–conc. HCl; cf. Weber *et al.*, A., 1898, i, 60), new m.p. 249—250° (dibenzoate, new m.p. 233—234°), is proved by (i) conversion of the βε-diacetate, new m.p. 264—265°, by boiling CH_2PhCl–KOH–PhMe into *αγδζ-dimethylenedulcitol βε-(CH$_2$Ph)$_2$ ether*, m.p. 164°, which is hydrolysed to dulcitol βε-$(CH_2Ph)_2$ ether, m.p. 168—169°, by HCl–aq. EtOH at 100° and regenerated therefrom by 37% CH_2O–conc. HCl–dioxan at 100°, and (ii) the stability of the *βζ-di*-p-*toluenesulphonate*, darkens at 220°, towards boiling NaI–Ac_2O. M.p. are corr.

R. S. C.

Structure of βγδε-di*iso*propylidene-*L*-fucitol. A. T. Ness, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 982—985).—*L*-Fucitol and HCl–$COMe_2$ at 20° give the *βγδε-(CMe$_2$)$_2$* derivative (**I**), m.p. 59—60°, [α] +11·7° in EtOH (*α-acetate*, m.p. 46—47°, [α] +26·1° in $CHCl_3$). The *α-benzoate*, m.p. 56·5—58°, [α] +18·7° in $CHCl_3$, of (**I**) in boiling 80% AcOH gives *L-fucitol α-benzoate* (**II**), m.p. 177—178°, [α] +4·30° in C_5H_5N, and slowly consumes 3 HIO_4 in aq. dioxan (no CH_2O formed) by hydrolysis to (**II**) and oxidations thereof. In AcOH, (**II**) rapidly consumes 3 equivs. of $Pb(OAc)_4$ and then, by oxidation of HCO_2H, slowly 2 further equivs.; CH_2O is not produced. With BzCl– or Ac_2O–C_5H_5N at room temp., (**II**) gives *L-fucitol pentabenzoate*, m.p. 149—150°, [α] −5·96° in $CHCl_3$, or *α-benzoate βγδε-tetra-acetate*, m.p. 116—117°, [α] +18·6° in $CHCl_3$, respectively. With *p*-$C_6H_4Me{\cdot}SO_2Cl$–C_5H_5N at 0°, later 23—24° and 40°, (**II**) gives *L-fucitol α-benzoate tri-* (22%), m.p. 155—157°, [α] +13·8° in $CHCl_3$, and *βγδε-tetra*-p-*toluenesulphonate*, m.p. 143—145°, [α] +18·0° in $CHCl_3$. (**I**) yields similarly *βγδε-diisopropylidene*-L-*fucitol* α-p-*toluenesulphonate*, m.p. 78—79°, [α] +19·7° in $CHCl_3$, and thence (NaI–$COMe_2$; 100°) *α-iodide*, m.p. 35—36°, [α] +28·9° in $CHCl_3$, which with H_2–Raney Ni in MeOH–H_2O–NaOH gives *αζ-bisdeoxy-βγδε-diisopropylidene-dulcitol* (**III**) (94%), m.p. 63—64°, α 0° in $CHCl_3$ (crystallo-optical data given), hydrolysed by boiling 80% AcOH to *αζ-bisdeoxy-dulcitol* (38%), m.p. 183—184°, α 0° in EtOH (consumes 3 $NaIO_4$, giving 2 HCO_2H). *βγδε-Diisopropylidenedulcitol* αζ-iodide is similarly reduced to (**III**). M.p. are corr. [α] are $[\alpha]_D^{20}$.

R. S. C.

Keten acetals. IX. Keten dialkyl acetals. S. M. McElvain and P. M. Walters (*J. Amer. Chem. Soc.*, 1942, **64**, 1059—1060; cf. A., 1942, II, 227).—Pr$^{\alpha}_2$, b.p. 94—95°/19 mm., *Bu$^{\beta}_2$*, b.p. 109—110°/19 mm., and *diisoamyl bromoacetal*, b.p. 137—139°/20 mm., are obtained from $CH_2{:}CH{\cdot}OAc$ and Br in ROH (50—60% yield) or $CHMe(OR)_2$ and Br, and with KOBu$^{\gamma}$–Bu$^{\gamma}$OH give *keten Pr$^{\alpha}_2$* (52%), b.p. 58—59°/16 mm., 153—154°/760 mm., *Bu$^{\beta}_2$* (47%), b.p. 76—77°/17 mm., 180—181°/760 mm., and *diisoamyl acetal* (51%), b.p. 105—106°/17 mm., 210—211°/760 mm., respectively.

R. S. C.

Esters of thiodiglycol. W. R. Clayton and E. E. Reid (*J. Amer. Chem. Soc.*, 1942, **64**, 908—909).—Thiodiglycol (purification described) has m.p. −10°, b.p. 147·5°/6 mm., is stable at 180°, is decomposed by 0·1—1N-NaOH, $Pb(OAc)_2$, or $Cu(NO_3)_2$ at 100°, but is unaffected by solid NaOH at 140°, $Ba(OH)_2$, CaO, or Al_2O_3 at 180°. With $(RCO)_2O$ or RCO_2H at 150—160° it gives the diformate, m.p. −15·5°, b.p. 134·5°/8 mm., diacetate, b.p. 139·5°/8 mm., *dipropionate*, m.p. −23°, b.p. 158°/8 mm., *dibutyrate*, m.p. −28°, b.p. 172°/8 mm. [also obtained from $S[(CH_2)_2{\cdot}Cl]_2$ (**I**) and Pr$^{\alpha}CO_2K$], *diisovalerate*, b.p. 181—182°/8 mm. [also obtained from (**I**)], and *di*-n-*hexoate*, m.p. 7°, b.p. 207°/7 mm. With $NPhMe_2$–$ZnCl_2$ at 120—160° it gives an oil, b.p. 204—210°/8 mm. $(Cl{\cdot}[CH_2]_2)_2SO$ does not react with KOAc in boiling AcOH or EtOH, but the sulphone and KOAc– or Bu$^{\beta}CO_2K$–AcOH gives oils.

R. S. C.

Potassium trimethyl orthosilicate. B. Helferich and K. Krenkler (*Ber.*, 1942, **75**, [*B*], 530—531).—*K Me$_3$ orthosilicate* is obtained by boiling $Si(OMe)_4$ (0·2 mol.) with solid, finely powdered anhyd. KOH (0·1 mol.) for 1 hr. and treating the supernatant liquid with $Si(OMe)_4$ (0·1 mol.); the cryst. product is washed with dry C_6H_6.

H. W.

Products of the conjoint action of sulphur dioxide and chlorine on aliphatic hydrocarbons in ultra-violet light. III. Sulphochlorination of *iso*butane and formation of isomerides during the sulphochlorination and chlorination of gaseous hydrocarbons. F. Asinger and F. Ebeneder (*Ber.*, 1942, **75**, [*B*], 344—349).—Sulphochlorination of $CHMe_3$ gives iso*butane-α-sulphonyl chloride* (**I**), b.p. 87°/15 mm. (corresponding cyclo*hexylamide*, m.p. 45°), in ~75% yield. Other products are a mixture of chloro*iso*butanesulphonyl chlorides and a little *β-methylpropane-αγ-disulphonic anhydride*, m.p. 188°

(corresponding *dianilide*, m.p. 118°; H of CH does not appear to be replaced). (**I**) is also obtained from Cl_2 and the corresponding thiocyanate. *β-Methylpropane-β-sulphonyl chloride*, b.p. 80°/15 mm. cannot be obtained by the thiocyanate or thiocarbamide method but is derived from $Bu^{\gamma}SO_3H$ and PCl_5. The same relationships appear to exist in the chlorosulphonation of C_3H_8 and n-C_4H_{10} in CCl_4 at ~20—30° as in the direct chlorination of these hydrocarbons under similar conditions or in the gas phase at 300° if an excess of hydrocarbon is present. This is true also for n- and *iso*-C_4H_{10} and n- and *iso*-C_5H_{12} except that *tert.* H is replaced by Cl but not by SO_2Cl. With a deficiency of hydrocarbon sulphochlorination is the simpler process since *gem*- and *αβ*-disubstitution are not observed. H. W.

Di[alkylsulphon]imides. B. Helferich and H. Flechsig (*Ber.*, 1942, **75**, [*B*], 532—536).—Gradual simultaneous addition of $MeSO_2Cl$ and 5N-NaOH to $MeSO_2{\cdot}NH_2$ in H_2O at ≯8° gives *dimethanesulphonimide* (anhyd.), b.p. 170°/0·5 mm. (also $+2H_2O$), which behaves as a strong acid, giving anhyd. *K*, *NH*$_4$, *Sr*, *Pb*, *Ti*^{I}, and C_5H_5N salts, Li ($+H_2O$), Na ($+H_2O$), Ba ($+2H_2O$), Cu ($+4H_2O$), Ni ($+4H_2O$), Co ($+4H_2O$), Mn ($+4H_2O$), and Cd ($+4H_2O$) salts. Simultaneous addition of $EtSO_2Cl$ (2 mols.) and 5N-NaOH (4 mols.) to NH_4Cl (1 mol.) in H_2O so that the solution is slightly alkaline gives *diethanesulphonimide*, m.p. 78·5—79° (*Na* salt, m.p. 157—158°), which can be accurately titrated with NaOH in presence of Me-orange. *Di-n-butanesulphonimide*, m.p. 84—85° (*Na* salt), is described. *Di-n-hexane-*, m.p. 88—89°, and *di-n-butane-*, m.p. 98°, *-sulphonimide* give *Na* salts which foam strongly in H_2O. $MeSO_2{\cdot}NH_2$, $EtSO_2Cl$, and 5N-NaOH yield *methanesulphonethanesulphonimide*, m.p. 103—104° [*Na* salt ($+1H_2O$), m.p. 163°]. cyclo*Hexanesulphonmethylsulphonimide*, m.p. 94—95°, is obtained analogously using $MeSO_2Cl$. H. W.

Acids and bases in organic chemistry. D. Davidson (*J. Chem. Educ.*, 1942, **19**, 154—160). L. S. T.

Ether-like compounds. XXVI. Rate of reaction and intramolecular forces. M. H. Palomaa [with T. Kaski, R. Korte, and T. A. Siitonen] (*Ber.*, 1942, **75**, [*B*], 336—339).—Measurements of the rates of esterification of $CH_2Cl{\cdot}CO_2H$ and $Cl{\cdot}[CH_2]_2{\cdot}CO_2H$ (in comparison with $OMe{\cdot}[CH_2]_2{\cdot}CO_2H$) and of the hydrolysis of $CH_2Cl{\cdot}CO_2Me$, $Cl{\cdot}[CH_2]_2{\cdot}CO_2Me$, $Cl{\cdot}[CH_2]_3{\cdot}CO_2Me$, $Cl{\cdot}[CH_2]_3{\cdot}CO_2Et$, and $Br{\cdot}[CH_2]_3{\cdot}CO_2Et$ show that Cl causes a more pronounced min. than ethereal O in the rate of catalytic esterification and hydrolysis. This effect, as with O, is most pronounced in the β-position. Cl with at. refraction 5·957 causes a less pronounced min. than Br with at. refraction 8·748. H. W.

Polymerisation of methyl methacrylate under the influence of benzoyl peroxide.—See A., 1942, I, 332.

Cerebrosides. XVII. Occurrence of a hexacosenoic acid amongst the fatty acids of cerebroside of brain. E. Klenk and E. Schumann (*Z. physiol. Chem.*, 1942, **272**, 177—188).—Cerebronic acid consists almost entirely of α-hydroxytetracosanoic acid but lignoceric acid is a mixture, probably of C_{22}, C_{24}, and C_{26} acids. The isolation by esterification, fractionation, and, in some cases, hydrogenation of a hexacosenoic acid, m.p. 45·0—45·5°, nervonic, and other (impure) acids (C_{16} to more than C_{26}) from the unsaturated acids of cerebrosides is described. W. McC.

Autoxidation of oxygen-active acids. II. Viscosimetric analysis of the addition of oxygen to the methyl esters. W. Treibs (*Ber.*, 1942, **75**, [*B*], 331—335; cf. A., 1942, II, 277).—Determinations of η of Me linolenate (**I**), linoleate (**II**), oleate, ricinoleate, *iso*elæostearate, α-elæostearate (**III**), glyceryl dilinolenate, linoleate, and trielæostearate show a diminution with increasing no of isolated and increase with increasing no. of conjugated double linkings. The course of autoxidation of the esters is viscosimetrically analysed by observing the rate of rise of the ester in a narrow strip of filter-paper. (**III**) is shown to be immediately converted by O_2 into a polymeric monoperoxide whereas (**I**) and (**II**) give monomeric monoperoxides; polymerisation and loss of H_2O accompany further addition of O. H. W.

Derivatives of octadecenoic acids. I. *p*-Phenylphenacyl esters. II. *S*-Benzylthiuronium salts. J. P. Kass, J. Nichols, and G. O. Burr (*J. Amer. Chem. Soc.*, 1942, **64**, 1061—1062).—*p*-Phenylphenacyl oleate (**I**), m.p. 61—62° (lit. 60·5°), elaidate (**II**), m.p. 72—73° (lit. 73·5°), linoleate, m.p. 37—37·5° (clear at 46·5—47°), linolelaidate, m.p. 73—75°, linolenate, m.p. 37·5—38° (clear at 38—39°), β-elæostearate, m.p. 89—90°, and *θικλ*-tetrabromostearate, m.p. 107—108°, and the corresponding *S*-benzylthiuronium salts, m.p. 125—125·5°, 123·5—125°, 122—123°, 122—124°, 115—130°, and 129—130°, respectively, are prepared. Of the unsaturated compounds only (**I**) and (**II**) have the correct I val. The salts are very unstable. R. S. C.

Branched-chain fatty acids. I. Synthesis of ρ-methyloctadecoic acid. J. Cason (*J. Amer. Chem. Soc.*, 1942, **64**, 1106—1110).—$CH_2Bu^{\beta}Br$ with Mg and then $CdCl_2$ in Et_2O gives $Cd(CH_2Bu^{\beta})_2$ (**I**), which with $CO_2Me{\cdot}[CH_2]_2{\cdot}COCl$ [prep. from $(CH_2{\cdot}CO)_2O$ (**II**) by way of the Me H ester, m.p. 53—57°, b.p. 110—111°/2 mm., modified], b.p. 85—87°, gives, after boiling, *Me γ-keto-ζ-methyl*-n-*octoate*, b.p. 122—125°/13 mm. (*semicarbazone*, sinters at 70°, m.p. 78—84°), hydrolysed by N-NaOH at 60±5° to the *acid*, m.p. 48—50°, b.p. 134°/2 mm. [*semicarbazone*, m.p. varies, 138—140° (decomp.)], which is obtained in poor yield from (**I**) and (**II**). Clemmensen reduction then gives $Bu^{\beta}{\cdot}[CH_2]_4{\cdot}CO_2H$, b.p. 103—105°/2 mm., the Et ester, b.p. 102°/12 mm., of which with Na–EtOH gives $Bu^{\beta}{\cdot}[CH_2]_5{\cdot}OH$ (**III**) (57%), b.p. 100°/13 mm., also obtained from $CH_2Bu^{\beta}{\cdot}MgBr$ by $(CH_2)_2O$ by way of $Bu^{\beta}{\cdot}[CH_2]_3{\cdot}OH$, b.p. 98—101°/45 mm., and *ζ-methyl*-n-*hexyl bromide*, b.p. 83°/45 mm. With 48% HBr, (**III**) gives *θ-methyl*-n-*octyl bromide*, b.p. 92—93°/12 mm., and thence $Cd([CH_2]_5{\cdot}Bu^{\beta})_2$, which with $CO_2Et{\cdot}[CH_2]_8{\cdot}COCl$ (modified prep.), b.p. 171—172°/12 mm., gives *Et ι-keto-ρ-methyl*-n-*octadecoate* (46%; 20% obtained by the MgBr derivative), b.p. 197°/1—2 mm. Hydrolysis then gives the *CO-acid*, m.p. 73·5—74·5° (*semicarbazone*, m.p. 97·5—97·7°), reduced (Clemmensen) to *ρ-methyloctadecoic acid*, m.p. 67·0—67·6° (*Pb* salt; *amide*, m.p. 100·2—101·3°; *tribromoanilide*, m.p. 112·0—112·5°), purified by way of the *Me* ester, m.p. 26—28°, b.p. 171—172°/1—2 mm. M.p. are corr. R. S. C.

Cardiolipin, $[\alpha]_D$ +7·0° in EtOH, from ox heart.—See A., 1942, III, 577.

Action of ethyl orthoformate on diacetyl and acetylacetone. L. N. Parfentiev and A. M. Mirzaev (*J. Gen. Chem. Russ.*, 1941, **11**, 707—712).—$CH(OEt)_3$ condenses with Ac_2 in presence of H_2SO_4 to *diacetyl tetra-acetal*, b.p. 51—52°/21 mm. $CH(OEt)_3$ and CH_2Ac_2 give a mixture containing *diethoxydimethylallene*, b.p. 128—129° (*tetrabromide*, an oil), formed by loss of EtOH from the tetra-acetal first produced, also a *solid*, m.p. 39°, b.p. 140—141°/20 mm., regarded as $CH(CHAc_2)_3$. G. A. R. K.

Synthesis of α-bromo-β-methoxy-*n*-butyric acid. H. E. Carter and L. F. Ney (*J. Amer. Chem. Soc.*, 1942, **64**, 1223—1224).—$CHMeBr{\cdot}CHBr{\cdot}CO_2Et$ (1 mol.) and NaOMe (1·25 mol.) (1 mol. gives mainly $CHMe{:}CBr{\cdot}CO_2Et$) in MeOH at −5° to 25° give $OMe{\cdot}CHMe{\cdot}CHBr{\cdot}CO_2Et$ (80—90%), b.p. 90—100°/18 mm., converted by aq. NaOH at 15—20° into the acid and thence *allo*threonine (best method of prep.). R. S. C.

Preparation and reactions of acetopyruvic (αγ-diketo-*n*-valeric) acid. A. L. Lehninger and E. J. Witzemann (*J. Amer. Chem. Soc.*, 1942, **64**, 874—878).—When $Et_2C_2O_4$ is condensed with $COMe_2$ and NaOEt, and the resultant $CHAc{:}C(ONa){\cdot}CO_2Et$ is treated in H_2O with 1·00 mol. of N-NaOH, 70% of $CH_2Ac{\cdot}CO{\cdot}CO_2H$, m.p. 98° (corr.) (*Cu* salt), is obtained. With 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$,HCl in hot EtOH it gives 1-2′ : 4′-*dinitrophenyl-5-methylpyrazole-3-carboxylic acid*, m.p. 239—241° (corr.). In excess (≮2 mols.) of aq. NaOH it is hydrolysed to $H_2C_2O_4$ and $COMe_2$, the (unimol.) rate depending on the [NaOH]. It is stable in aq. acid at ≯38° and in H_2O or in vac. at 0°. It is dibasic (potentiometric titration), having k_1 2·6 × 10^{-3} and k_2 3·2 × 10^{-9}. With $KMnO_4$ (0·4 mol.) in H_2SO_4 it gives $COMe_2$, $H_2C_2O_4$, CO_2, and (?) $CH_2Ac{\cdot}OH$ and $AcCO_2H$, by way of, mainly, $CH_2Ac{\cdot}CO_2H$. In very dil. alkali it gives CO_2 and AcOH, but in more conc. alkali gives also $H_2C_2O_4$ by way of $Me{\cdot}[CO]_2{\cdot}CO_2H$. Its stability is too great to permit it to function as a biological intermediate. R. S. C.

Action of monoethanolamine on ethyl bromomalonate. C. B. Kremer, M. Meltsner, and H. Hindin (*J. Amer. Chem. Soc.*, 1942, **64**, 1010).—$CHBr(CO_2Et)_2$ and $NH_2{\cdot}[CH_2]_2{\cdot}OH$ at the b.p. give $CH_2(CO_2Et)_2$. R. S. C.

Preparation of dicarboxylic acids related to civetone. I. Preparation of *cis*- and *trans*-Δ$^{\iota}$-oetadecene-αω-dicarboxylic acid. L. Ruzicka, P. A. Plattner, and W. Widmer (*Helv. Chim. Acta*, 1942, **25**, 604—620).—Condensation of Me undecenoate by Na in xylene gives ~50% of *Δ$^{\alpha\chi}$-docosadien-λ-ol-μ-one* (**I**), m.p. 45—47° (softens at 41·5°), which does not give a yellow colour with $C(NO_2)_4$, and ~2% of the corresponding *diketone* (**II**), m.p. 52—53° [*phenylosazone*, m.p. 69—70° (softens at 65°), obtained from (**I**) or (**II**); *disemicarbazone*, m.p. 236—238° (decomp.)]. (**II**) is oxidised by H_2O_2 and alkali to undecenoic acid. Catalytic reduction (Rancy Ni) of (**I**) or (**II**) affords β-, m.p. 128—129°, and α-, m.p. 82·5—83·5°, *-docosane-λμ-diol*. Na and EtOH reduce (**I**) to β- (**III**), m.p. 114·5—115·5°, and α- (**IV**), m.p. 62—63° (softens at 60°), *-Δ$^{\alpha\chi}$-docosadiene-λμ-diol* with some *Δ$^{\alpha\chi}$-docosadien-λ-ol*, m.p. 54—56°. Better results are obtained by the reduction of (**I**) or (**II**) by Al(OPr$^{\beta}$)$_3$ in Pr$^{\beta}$OH. (**III**) gives a :*CMe*$_2$ derivative, b.p. 151—153°/0·03 mm., and a *diacetate* (**V**), b.p. 210° (bath)/0·02 mm. The :*CMe*$_2$ derivative, b.p. 156—157°/0·07 mm., and *diacetate* (**VI**) of (**IV**) are described. Ozonisation of (**V**) in CCl_4 and oxidation of the product with $KMnO_4$ leads to *β-ικ-dihydroxyoctadecane-αω-dicarboxylic acid* (**VII**), m.p. 142·5—144° (*Me*$_2$ ester, m.p. 94—95°), whilst similar treatment of (**VI**) leads to the corresponding *α-acid* (**VIII**), m.p. 119—123° after softening at 110° (*Me*$_2$ ester, m.p. 69—71·5°). (**VII**) and 33% HBr–AcOH at 100° give the (impure) *β-ικ-dibromo-octadecane-αω-dicarboxylic acid*, m.p. 78—82° [*Me*$_2$ ester (**IX**), m.p. 35—36°]; the corresponding *α-Br*$_2$-acid, m.p. 98—100° (softens at 81°), and its *Me*$_2$ ester (**X**), m.p. 57·5—58·5° (softens at 55°), are described. (**IX**) is converted by NaI and Zn dust in boiling $COMe_2$ followed by CH_2N_2 into *Me*$_2$ *β-Δ$^{\iota}$-octadecene-αω-dicarboxylate*, m.p. 30·5—31·5° [*acid* (**XI**), m.p. 80—81°], hydrogenated (Raney Ni in EtOH) and

then hydrolysed to octadecane-$\alpha\sigma$-dicarboxylic acid, m.p. 124—125° (Me_2 ester, m.p. 65—65·5°). Similarly (**X**) affords *Me_2 α-Δ$^{\iota}$-octadecene-ασ-dicarboxylate*, m.p. 42·5—44·5° (*acid*, m.p. 112·5—113·5°). Ozonisation of (**XI**) gives sebacic acid. M.p. are corr. H. W.

Tracer studies with radioactive carbon and hydrogen. Synthesis and oxidation of fumaric acid. M. B. Allen and S. Ruben (*J. Amer. Chem. Soc.*, 1942, **64**, 948—950).—^{11}C is converted by way of $^{11}CO_2$, K^{11}CN, and $(CH_2{\cdot}^{11}CN)_2$ into fumaric acid (**I**), $(CH{\cdot}^{11}CO_2H)_2$. When this is oxidised by $KMnO_4$–H_2SO_4 (to give $3CO_2 + 1HCO_2H$), the HCO_2H produced is not radioactive and thus originates in the CH of (**I**). When non-radioactive (**I**) is oxidised in a solution containing ^3H_2O (no exchange of H occurs), the HCO_2H is not radioactive. The C–H linking of the CH of (**I**) thus remains intact. The mechanism of oxidation is thus: (**I**) → $CO_2H{\cdot}C(OH){:}CH{\cdot}CO_2H$ → CO_2 + $OH{\cdot}CH(CO_2H)_2$ → CO_2 + $CHO{\cdot}CO_2H$ → HCO_2H + CO_2. R. S. C.

Modern methods of preparative organic chemistry. XVI. Diene syntheses. K. Alder (*Angew. Chem.*, 1942, **55**, 53—58).—A lecture.

Components of Fehling's solution.—See A., 1942, I, 334.

Carbonyl compounds as oxidising agents. H. Adkins (*J. Chem. Educ.*, 1942, **19**, 218—221). L. S. T.

Formaldehyde condensation as organic autocatalysis. W. Langenbeck [with W. Sander and F. Kühn] (*Naturwiss.*, 1942, **30**, 30—34).—The autocatalytic character of the condensation of CH_2O is established kinetically in presence of $CO(CH_2{\cdot}OH)_2$ (**I**), $OH{\cdot}CH_2{\cdot}CHO$ (**II**), fructose, $CHPhBz{\cdot}OH$–CH_2O compound (**III**), glucose, $CHPhBz{\cdot}OH$ (**IV**), anisoin, and acetoin. The individual catalysts differ only in their period of incidence and the max. acceleration is the same for each. The most active catalysts are (**I**) and (**II**) and these are doubtless the actual autocatalysts since there is no induction period. (**III**) is more active than (**IV**). (**III**) is $OH{\cdot}CH_2{\cdot}CPhBz{\cdot}OH$ since it is oxidised by $Pb(OAc)_4$ to Bz_2 and CH_2O and its oxime is transformed by Ac_2O into PhCN and $CH_2Bz{\cdot}OAc$. The mechanism of the action is discussed. H. W.

Formation and decomposition of hexamethylenetetramine. E. Baur and W. Rüetschi (*Helv. Chim. Acta*, 1941, **24**, 754—767).—The reaction between CH_2O and NH_3 in presence of an excess of either reactant and at temp. between 0° and 50° is shown by acidimetric titration in presence of phenol-red to be probably of the third order and to proceed mainly through $(CH_2{\cdot}NH)_3$. The synthesis of $(CH_2)_6N_4$ from $(NH_4)_2SO_4$ and CH_2O in presence of an OAc′–AcOH buffer has been followed at temp. between 0° and 60° by argentometric determination of CH_2O and measurement of p_H by the quinhydrone electrode and the decomp. of $(CH_2)_6N_4$ has been investigated similarly. At higher temp. $(CH_2)_6N_4$ fulfils the conditions of Guldberg's theorem of the independence of equilibrium on the direction, whereas at lower temp., abnormalities are observed in the sense of Baur's theorem. H. W.

Novel type of Cannizzaro reaction. E. M. Fry, E. J. Wilson, jun., and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 872—873).—In N-NaOH at 100°, *L′*-methoxy-*L*-methyldiglycollic dialdehyde (obtained from α-methyl-*L*-rhamnopyranoside) consumes 1 mol. of NaOH and undergoes intramol. disproportionation, giving $CO_2H{\cdot}CH(OMe){\cdot}O{\cdot}CHMe{\cdot}CH_2{\cdot}OH$ (60%) and $OH{\cdot}CH_2{\cdot}CH(OMe){\cdot}CHMe{\cdot}CO_2H$ (40%). These products could not be isolated as such but are identified by hydrolysis by aq. HCl at 100° to $CHO{\cdot}CO_2H$ (semicarbazone), $CH_2(CH_2{\cdot}OH)_2$ (diphenylurethane), $CHO{\cdot}CH_2{\cdot}OH$ (phenylosazone), and *L*-lactic acid (Zn salt). R. S. C.

Manufacture of unsaturated ketones.—See B., 1942, II, 251.

Condensation of ketones with alcohols in the presence of mixed catalysts. V. N. Ipatiev and V. Haensel (*J. Org. Chem.*, 1942, **7**, 189—198).—Ketones with reactive ·COMe and alcohols with the terminal group $\cdot CH_2{\cdot}OH$ or $\cdot CHMe{\cdot}OH$ give large yields of higher ketones at >200°/1—50 atm. These ketones contain the no. of C atoms equiv. to the sum of the C atoms of the original ketone and alcohol. Only catalysts having both dehydrogenating and dehydrating properties can effect the condensation. The extent of the reaction and purity of the product depend largely on the initial alcohol : ketone ratio. There is no conclusive proof of the mechanism of the change. An intermediate H disproportionation reaction is involved and a mol. of H_2O is eliminated from ketone + alcohol. Primary alcohols (**I**) and ketones afford higher ketones by a similar mechanism. (**I**) alone in the presence of the same catalyst produce esters which are formed through a Cannizzaro reaction. The following changes are described. $Pr^{\beta}OH$ + $COMe_2$ to $COMeBu^{\beta}$ and $COBu^{\beta}_2$; $Pr^{\beta}OH$ + COMeEt to $COPr^{\alpha}{\cdot}CH_2{\cdot}CHMeEt$, $COMe{\cdot}CH_2{\cdot}CHMeEt$, and $COEtBu^{\beta}$; $COMe_2$ + $CHPr^{\beta}{\cdot}OH$ to $COPr^{\beta}_2$ with a little $COMeBu^{\beta}$; $Pr^{\beta}OH$ + *cyclo*hexanone to (?) *cyclo*hexylacetone; $Bu^{\alpha}OH$ + $COMe_2$ to $COMe{\cdot}C_6H_{11}$ + $PrCO_2Bu^{\alpha}$; $COMe_2$ + $Pr^{\alpha}OH$ to $COMeBu$ + $EtCO_2Pr^{\alpha}$; EtOH + $COMe_2$ to $COMePr^{\alpha}$ and $COPr^{\alpha}_2$; $Bu^{\beta}OH$ to $Pr^{\beta}CO_2Bu^{\beta}$ with a little $Pr^{\beta}CHO$; $Pr^{\alpha}OH$ to $COEt_2$, EtCHO $CHEt_2{\cdot}OH$, and $EtCO_2Pr^{\alpha}$. H. W.

Dipole moments and structures of diketen, and of acid anhydrides and related oxygen and sulphur compounds.—See A., 1942, I, 289.

Behaviour of γ-diketones. I. H. Hunsdiecker (*Ber.*, 1942, **75**, [*B*], 447—454).—Various methods of prep. are discussed and illustrated. 5-Methylfurfuraldehyde, COMePr, and dil. NaOH at room temp. slowly afford 5-methylfurfurylidenemethyl Pr ketone, b.p. 138·5°/5 mm., reduced by Na–Hg and EtOH at 10—15° but not catalytically (PtO_2 or Pd–$BaCO_3$) to 5-methyl-2-γ-ketohexylfuran, b.p. 89—90°/1·5 mm., which is converted according to Wolff–Kishner but not Clemmensen into 5-methyl-2-*n*-hexylfuran, b.p. 96°/20 mm. This is transformed by aq. AcOH–H_2SO_4 at 120° into *undecane-βε-dione*, m.p. 33°. Furfurylideneacetone in converted by boiling HCl–EtOH into *γζ-diketo-octoic acid* (**I**), m.p. 77—78°, with large amounts of resin which is reduced if the ketone is added slowly to the gently boiling acid. Similarly furylidenemethyl Et ketone gives γζ-diketononoic acid (**II**). The following are obtained by electrolysis between Pt electrodes of solutions of diketo-acids and fatty acids which have been neutralised to a small extent by NaOMe: (**I**) with $EtCO_2H$ gives *nonane-βε-dione*, b.p. 113°/15 mm., with $Pr^{\alpha}CO_2H$ *decane-βε-dione*, b.p. 132°/17 mm., with $Bu^{\alpha}CO_2H$ *undecane-βε-dione*, b.p. 141°/14 mm., m.p. 33°, with $Bu^{\beta}CO_2H$ *ι-methyldecane-βε-dione*, b.p. 130°/13 mm., with *n*-$C_5H_{11}{\cdot}CO_2H$ *dodecane-βε-dione*, b.p. 148°/12 mm., m.p. 40·5°, with *n*-$C_7H_{15}{\cdot}CO_2H$ *tetradecane-βε-dione*, b.p. 158°/14 mm., m.p. 51°, with lauric acid *octadecane-βε-dione*, b.p. 170°/1 mm., m.p. 71°, with $OMe{\cdot}[CH_2]_4{\cdot}CO_2H$ *λ-methoxyundecane-βε-dione*, b.p. 167°/13 mm., m.p. 23°, with $CO_2H{\cdot}[CH_2]_2{\cdot}CO_2Me$, *Me εθ-diketodecoate*, b.p. 195°/18 mm., with $CO_2H{\cdot}[CH_2]_4{\cdot}CO_2Me$, *Me ηκ-diketododecoate*, b.p. 164°/1 mm., m.p. 32°, with *γ-iso*amyloxybutyric acid, *ι*-iso*amyloxydecane-βε-dione*, b.p. 139°/2 mm., whilst (**II**) and $Bu^{\alpha}CO_2H$ yield *dodecane-γζ-dione*, b.p. 150°/16 mm., m.p. 41°. *Tetradecane-βεκν-tetraone*, m.p. 105°, and *hexadecane-γζλχ-tetraone*, m.p. 116°, are derived from (**I**) and (**II**) respectively. Interaction of $CHNaAc{\cdot}CO_2Et$ (10% excess) with the requisite acid chloride gives a 75—85% yield of the acylacetoacetate, converted by NaOMe in MeOH at room temp. into the acylacetic ester (**III**); thus are obtained *Me* iso*valeryl-*, b.p. 64°/2 mm., *Me hexoyl-*, b.p. 109°/11 mm., *Me heptoyl-*, b.p. 115°/7 mm., and *Me phenylacetyl-*, b.p. 125°/3 mm., *-acetate*. The Na derivatives of (**I**) are condensed with $COMe{\cdot}CH_2Br$ ($COPh{\cdot}CH_2Br$, $CHMeBr{\cdot}COMe$, etc.), giving thus *Me-α-hexoyl-*, b.p. 143°/2·5 mm., *Me α-heptenoyl-*, b.p. 123°/0·5 mm., and *Me β-methyl-α-*iso*valerylævulate*, b.p. 142°/12 mm. H. W.

Manufacture of keto-alcohols.—See B., 1942, II, 251.

Keto-ethers. IX. Propoxymethyl alkyl (or phenyl) ketones. H. R. Henze, (Miss) V. B. Duff, W. H. Matthews, jun., J. W. Melton, and E. O. Forman (*J. Amer. Chem. Soc.*, 1942, **64**, 1222—1223; cf. A., 1941, II, 351).—*CH_2Cl Pr^{α}* [prep. from $Pr^{\alpha}OH$ by $(CH_2O)_3$– or 60% aq. CH_2O–HCl gas; 60% yield], b.p. 26—28°/32 mm., 110°/755 mm., and *Pr^{β} ketone* (prep. from $Pr^{\beta}OH$ by 36% aq. CH_2O–HCl; 49% yield), b.p. 36°/45 mm., 101°/750 mm., with anhyd. CuCN in boiling Et_2O gives n- (55%), b.p. 56°/40 mm., 152°/751 mm., and iso-*propoxyacetonitrile*, b.p. 74°/53 mm., 145—146°/748 mm., respectively, converted by MgRHal–Et_2O and then cold HCl into $OPr{\cdot}CH_2{\cdot}COR$. n- and iso-*Propoxymethyl alkyl* (or aryl) *ketone*, successively, are described in which R = Me, b.p. 49°/6 mm. (150°/763 mm.), 35°/10 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 144°), *Et*, b.p. 56°/4 mm., 47°/11 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 103°), *Pr^{α}*, b.p. 64°/4 mm., 56°/8 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 98°), *Pr^{β}*, b.p. 79°/60 mm., 42°/6 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 89°), *Bu^{α}*, b.p. 81°/12 mm., 63°/7 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 78°), *Bu^{β}* b.p. —, 56°/5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 95°), *CHMeEt*, b.p. —, 50°/5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 61°), n-, b.p. 120°/5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 73°), 83°/8 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 77°), and iso-*amyl*, b.p. 111°/26 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 79°), 83°/9 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 82°). *Ph* n-, b.p. 118°/6 mm., and iso-*propoxymethyl ketone*, b.p. 112°/6 mm., are also prepared. Temp. are corr. R. S. C.

Production of unsaturated amines.—See B., 1942, II, 251.

Alkylammonium borates.—See A., 1942, I, 335.

Ethanol- and chloroethyl-ammonium metallic chlorides.—See A., 1942, I, 337.

Cobaltous and chromic ethanolamine complexes.—See A., 1942, I, 337.

Derivatives of alcohol amines [hydroxyalkylamines].—See B., 1942, II, 252.

Copper, nickel, and uranyl compounds of ethylenediaminetetraacetic acid.—See A., 1942, I, 334.

Esters of choline and its homologues. II. S. I. Lurie, Z. I. Fedorova, and E. D. Volkova (*J. Gen. Chem. Russ.*, 1941, **11**, 739—744; cf. A., 1940, II, 156).—Halides of esters of choline and ethylcholine with substituted benzoic acids are cryst. and readily purified, but those of homocholine crystallise with difficulty and are hygroscopic. Alkylamine esters of *m*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$ are obtained in yields >82%, but those of *p*-nitro- and *p*-chloro-benzoic acid in

55—58% yield; this is explained on an electronic basis. Bromocholine bromide (I) and *p*-NHAc·C_6H_4·CO_2Ag (II) give *choline* p-*acetamidobenzoate bromide*, m.p. 257—258°. Chlorohomocholine bromide and (II) give *homocholine* p-*acetamidobenzoate chloride* and the *chloride* of *ethylhomocholine* p-*acetamidobenzoate*, hygroscopic crystals, is formed from (II) and chloroethylaminopropyl iodide; with EtBr this gives *ethylhomocholine* p-*acetamidobenzoate bromide* (IV), m.p. 211—212°, also obtained by the action of EtBr on the reaction product of γ-diethylaminopropyl chloride and *p*-NHAc·C_6H_4·CO_2H. (I) and *p*-NHBu·C_6H_4·CO_2Ag give *choline* p-n-*butylaminobenzoate bromide*, m.p. 163—164·5°. *Ethylhomocholine* p-*hydroxybenzoate iodide*, hygroscopic crystals, is obtained by the action of EtI on the product, m.p. 100—102°, formed by heating γ-diethylaminopropyl *p*-hydroxybenzoate. By a similar method *ethylhomocholine*-m-, pale cream crystals, m.p. 179°, and -p-*nitrobenzoate bromide*, pale cream crystals, m.p. 204—206°, have been obtained. (I) and *p*-C_6H_4Cl·CO_2Ag give *choline* p-*chlorobenzoate bromide*, m.p. 194—196°. *γ-Diethylaminopropyl* p-*chlorobenzoate* has m.p. 234—235°. (IV) causes intestinal peristalsis comparable with that due to eserine.

G. A. R. K.

Syntheses of aminopropanols. II. O. Hromatka (*Ber.*, 1942, **75**, [*B*], 379—383; cf. A., 1942, II, 278).—The prep. of γ-aminopropanols from CH_2:CH·CH_2·OH (I) and amines under the influence of alkali is a general reaction. Protracted heating of a suspension of sarcosine in (I) containing CH_2:CH·CH_2·ONa at 108° and esterification (MeOH–HCl) of the product gives *Me methyl-γ-hydroxypropylaminoacetate*, b.p. 133—138°/18 mm. (*benzoate hydrochloride*, m.p. 151—153°). Similarly Ph·$[CH_2]_2$·NH_2 affords *β-phenylethyl-γ-hydroxypropylamine*, b.p. 127—135°/0·7 mm. (*picrate*, m.p. 138°), and *β-phenylethyldi-γ'-hydroxypropylamine*, b.p. 187—190°/0·8 mm. NH_2Ph gives γ-hydroxypropylaniline, b.p. 140°/0·4 mm. (*picrate*, m.p. 113—114°). $NHEt_2$ and CH_2:CH·CHEt·ONa (II) in PhMe give NEt_2·$[CH_2]_2$·CHEt·OH [*styphnate*, m.p. 103° (vac.)], also obtained from OH·CHEt·$[CH_2]$·Cl (III) and $NHEt_2$. Similarly (II) and piperidine afford *α-piperidinopentan-γ-ol*, b.p. 115°/12 mm. [*styphnate*, m.p. 98—99°; p-*nitrobenzoate hydrochloride*, m.p. 174° (vac.)], obtained also from (III). γ-Piperidino-γη-dimethyl-Δ^5-octen-α-ol (*picrate*, m.p. 116°) is derived from geraniol.

H. W.

Optically active phenylurethane anæsthetics. M. S. Raasch and W. R. Brode (*J. Amer. Chem. Soc.*, 1942, **64**, 1112—1114).—*dl-α*-Piperidinopropane-*βγ*-diol (I) is resolved by *l*-menthoxyacetic acid in $COMe_2$ into the *l*- (*l*-menthoxyacetate, m.p. 106°, $[\alpha]_D^{24}$ −67° in EtOH) and d-*diols*, b.p. 137°/12 mm., $[\alpha]_D^{20}$ ±13·1° in EtOH, which afford the *l*-' (II), m.p. 96—98°, $[\alpha]_D^{24}$ −14·3° in H_2O, and d-*diphenylurethane hydrochloride* (III), +COMeEt, m.p. 98—99°, $[\alpha]_D^{24}$ +14·5°, and l- and d-*phenylurethane hydrochloride*, m.p. 187—188°, $[\alpha]_D^{21}$ −15·6°, $[\alpha]_D^{30}$ +15·7° in MeOH. By means of camphoric acid *dl*- gives *d*-, b.p. 156·5—157°, $[\alpha]_D^{26}$ +46·7° (d-*camphorsulphonate*, m.p. 126—127°, $[\alpha]_D^{24}$ +41·8° in EtOH), and l-*α-diethylaminopropan-β-ol*, b.p. 157°, $[\alpha]_D^{24}$ −46·2° in EtOH (l-*camphorsulphonate*, m.p. 125—126°, $[\alpha]_D^{24}$ −41·5° in EtOH), and thence the d- (IV) and l-*phenylurethane hydrochloride* (V), m.p. 165°, $[\alpha]_D^{24}$ +10·3° in EtOH. (II), (III), and the *dl*-isomeride, freed from COMeEt, have equal anæsthetic activity (rabbit's cornea), but +COMeEt the *l*-form is the most effective; intravenous toxicities are *l*- 25, *d*- = *dl*- 18 mg. per kg. body wt. The monophenylurethane of (I) is a weak anæsthetic, as also are (IV), (V), and the *dl*-isomeride, which have equal effect.

R. S. C.

Esters of *C*-dialkylglycines [α-amino*iso*butyric acids].—See B., 1942, II, 252.

Adsorption behaviour of fission products of proteins. II. Chromatography of aminodicarboxylic acids on alumina. F. Turba and M. Richter (*Ber.*, 1942, **75**, [*B*], 340—344).—Untreated Al_2O_3 is not active enough; its activity is greatly improved by pre-treatment with N-HCl but for full development requires the use of a 0·05N-AcOH–OAc' buffer with p_H 3·3. Under these conditions aspartic (I) and glutamic acid (II) are quantitatively adsorbed and can be completely recovered by elution with dil. alkali. They can thus be quantitatively separated from glycine, alanine, leucine, serine, arginine, histidine, tryptophan, proline, cystine, and methionine. They can also be separated from one another since (II) is quantitatively washed into the filtrate by N-AcOH–OAc' buffer whilst (I) is retained by the Al_2O_3, from which it is removed by dil. alkali.

H. W.

[Preparation of] aliphatic vinyl tertiary amides.—See B., 1942, II, 252.

Preparation of γ-alkylamides of glutamic acid. N Lichtenstein [with S. Gertner] (*J. Amer. Chem. Soc.*, 1942, **64**, 1021—1022).—Pyrrolidonecarboxylic acid with 17% aq. NH_2Me or 33% aq. $NHEt_2$ at 37° gives *glutam-γ-methyl-*, m.p. 192°, $[\alpha]_D^{26}$ +6·45°, and *-ethylamide*, m.p. 200°, $[\alpha]_D^{24}$ +6·25°, respectively, the structure of which is proved by non-formation of NH_2R by $Ba(OH)_2$ at 35—40° but liberation thereof by $Ca(OH)_2$ at 35—40° after hydrolysis by 20% HCl. The products give high Van Slyke vals., probably owing to formation of the γ-OH-acid and thence of the lactone.

R. S. C.

Preparation of monosubstituted ureas.—See B., 1942, II, 252.

Synthesis of a cyanogenetic substance by oxidation of formaldehyde and ammonia. R. Fosse, R. de Larambergue, and J. Gaiddon (*Compt. rend.*, 1941, **213**, 329—331).—Oxidation of a mixture of CH_2O and NH_3 with $KMnO_4$ and $(NH_4)_2SO_4$ does not give free HCN in appreciable amount but yields an intermediate which gives HCN when the solution is distilled and a ppt. of AgCN when heated with $AgNO_3$–HNO_3. Successive additions of $AgNO_3$ and HCl to the solution give free HCN, which is not liberated by HCl alone.

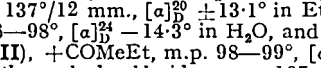
C. S.

II.—SUGARS AND GLUCOSIDES.

2 : 3-Dimethylrhamnose. O. T. Schmidt, E. Plankenhorn, and F. Kübler (*Ber.*, 1942, **75**, [*B*], 579—582).—*iso*Propylidenerhamnose, powdered KOH, and CH_2PhCl at 100° give 1 : 5-*dibenzyl*-2 : 3-*isopropylidenerhamnofuranose* (I), m.p. 104°, $[\alpha]_D^{20}$ +30·3° in $COMe_2$, with smaller amounts of an *isomeride*, m.p. 84°, $[\alpha]_D^{20}$ −15·44° in $COMe_2$. (I) is hydrolysed by 0·05N-HCl at 100° to 1 : 5-*dibenzylrhamnofuranoside*, m.p. 77·5°, $[\alpha]_D^{20}$ +48·2° in $COMe_2$, converted by Me_2SO_4–KOH at 50° into 1 : 5-*dibenzyl*-2 : 3-*dimethylrhamnofuranoside* (II), m.p. 119°, $[\alpha]_D^{20}$ +71·7° in $COMe_2$, which is transformed by H_2–PdO in MeOH into 2 : 3-*dimethylrhamnose* (III), b.p. 125—130°/0·01 mm., $[\alpha]_D^{23}$ +47·6° in H_2O; this with NHPh·NH_2 in AcOH under N_2 gives 3-*methylrhamnosephenylosazone*, m.p. 128—130° [or, hydrated, m.p. 118° (decomp.)], $[\alpha]_D^{20}$ +57° in C_5H_5N–EtOH (2 : 3) after 17 hr. (II) and boiling MeOH containing 1% of conc. HCl yield 5-*benzyl*-2 : 3-*dimethylmethylrhamnofuranoside*, m.p. 93°, $[\alpha]_D^{20}$ −72° in $COMe_2$, hydrogenated to 2 : 3-*dimethylmethylrhamnoside*, b.p. 100°/0·1 mm. (III) and azobenzoyl chloride in abs. C_5H_5N at 40° afford two cryst. *diesters*, $C_{31}H_{32}O_7N_2$, m.p. 241°, $[\alpha]_{6252}^{20}$ +33·7° in $CHCl_3$, and m.p. 165°, $[\alpha]_{6252}^{20}$ −3·5° in $CHCl_3$.

H. W.

Thiosugar of yeast. G. Wendt (*Z. physiol. Chem.*, 1942, **272**, 152—156; cf. A., 1926, 52, 96).—The methylthiolpentose (triacetate, m.p. 66—67°), obtained from the adenylmethylthiolpentose of yeast by acid hydrolysis, consumes 4 I when treated with HOI, yielding SMe·CH_2·$[CH(OH)]_3$·CO_2H, also obtained by oxidation with dil. HNO_3. The product of reduction with Hg–Na, SMe·CH_2·$[CH(OH)]_3$·CH_2·OH, m.p. 118°, contains no SH and is converted with consumption of 2 I into the corresponding sulphoxide, SOMe·CH_2·$[CH(OH)]_3$·CH_2·OH. With $Pb(OAc)_4$ the reduction product yields ~1 mol. of CH_2O whereas the pentose itself yields no CH_2O thus. The results indicate that the pentose probably is



Its configuration probably corresponds with that of *d*-ribose.

W. McC.

Synthesis of glucose and gentiobiose derivatives. D. D. Reynolds and W. O. Kenyon (*J. Amer. Chem. Soc.*, 1942, **64**, 1110—1112).—Addition of $COCl_2$–PhMe to *β-d*-glucose 1 : 2 : 3 : 4-tetra-acetate (I) and $CaSO_4$ in C_5H_5N gives *di*-1 : 2 : 3 : 4-*tetra-acetyl-* (82%), m.p. 198—199°, $[\alpha]_{5461}^{26.5}$ +12·15° in $CHCl_3$, converted by HBr–AcOH at room temp. into *di*-1-*bromo*-2 : 3 : 4-*triacetyl-β-d-glucosyl carbonate*, m.p. 147—148°, $[\alpha]_{5461}^{26.5}$ +258° in $CHCl_3$. With Ag_2O–$CaSO_4$–MeOH this gives *di*-2 : 3 : 4-*triacetyl-β-d-methylglucosidyl carbonate*, m.p. 191—192°, $[\alpha]_{5461}^{26}$ −75·0°, and with (I)–Ag_2O–$CaSO_4$–$CHCl_3$ gives *di*-1 : 2 : 3 : 4 : 2' : 3' : 4'-*hepta-acetyl-β-gentiobiosyl carbonate* (40%), m.p. 237—238°, $[\alpha]_{5461}^{26}$ −28·8° in $CHCl_3$, hydrolysed by NaOMe–MeOH–$CHCl_3$ at room temp. to gentiobiose (76%).

R. S. C.

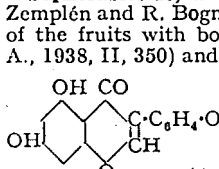
Synthesis of primverin, the principal glucoside of the primrose (*Primula officinalis*). F. Mauthner (*J. pr. Chem.*, 1941, [ii], **159**, 36—38).—*β*-Resorcylic acid and Me_2SO_4–aq. NaOH first at room temp. and then at the b.p. afford (after hydrolysis) the 4-Me ether, m.p. 158—159°, the Me ester, m.p. 48—49°, of which with α-acetobromoprimverose (Zemplén *et al.*, A., 1939, II, 99) and quinoline–Ag_2O yields primverin hexa-acetate, m.p. 210—211°, converted by NH_3–MeOH at 0° into primverin, m.p. 203—204°.

A. T. P.

Ganglioside; a new group of sugar-containing cerebral lipins. E. Klenk (*Z. physiol. Chem.*, 1942, **273**, 76—86; cf. *ibid.*, 1941, **270**, 185).—Ganglioside (I), decomp. ~205°, from the protagon fraction of brain, is a sugar-containing lipin, probably derived as follows: $C_{18}H_{36}O_2$ (stearic acid) (II) + $C_{18}H_{37}O_2N$ (sphingosin or related compound) (III) + $C_{10}H_{19}O_9N$ (neuramic acid) + $3C_6H_{12}O_6$ (galactose) (IV) = $C_{84}H_{118}O_{26}N_2$ (I) +$5H_2O$. Purification of (I) from cerebrosides and phosphatides is effected through decomp. of the Pb salt, followed by solvent extraction and chromatographic analysis. Purified (I) and boiling 10% H_2SO_4–MeOH give (II) + (III) (as sulphate) and (I)–10% HCl afford (IV).

A. T. P.

Sophorabioside, a new glucoside from *Sophora japonica*, L. G. Zemplén and R. Bognár (*Ber.*, 1942, **75**, [*B*], 482—489).—Extraction of the fruits with boiling EtOH yields sophoricoside (I) (Charaux, A., 1938, II, 350) and *sophorabioside* (II) but no sophoraflavonoloside (Rabaté *et al.*, A., 1938, II, 350). (I) is (*A*). (II) (anhyd.), softens at 240°, m.p. 248° (incipient decomp.), $[\alpha]_D^{19}$ −72·5° in C_5H_5N, (+$3H_2O$), m.p. 245—248° after softening at 150°, melting at 156—160° (decomp.), resolidifying at



(*A*.)

190—200°, and re-melting at 245—248°, $[\alpha]_D^{19}$ −66·3° in C_5H_5N, is hydrolysed by acids to genistein [triacetate, m.p. 205—206° (corr.)], *d*-glucose, and *l*-rhamnose. Ozonisation of (II) gives an amorphous biose (amorphous *acetate*, $[\alpha]_D^{20}$ −20·0° in $CHCl_3$). Oxidation of (II) by OI′ leaves the *l*-rhamnose component unchanged. Sophorabiose is therefore a rhamnosidoglucose different from rutinose and closely analogous to neohesperidose. (II) gives an *octa-acetate*, m.p. 254—255°, softens at 240°, $[\alpha]_D^{15}$ −52·7° in C_5H_5N. Methylation (Me_2SO_4 and warm NaOH) of (II) gives an amorphous product containing sugar which is hydrolysed by acids to 2 : 4 : 6-*trimethoxyphenyl* p-*hydroxybenzyl ketone*, m.p. 165·5—170·5° (corr.), identical with the compound obtained from (I) and by the Hoesch synthesis from 2 : 4 : 6-$C_6H_3(OMe)_3$ and *p*-OH·C_6H_4·CH_2·CN. With Me_2SO_4 and cold alkali (II) gives an amorphous product, hydrolysed to *genistein* 5 : 7-Me_2 *ether* (III), m.p. 266—266·5° [*acetate*, m.p. 187° (corr.), softens at 185°]. CH_2N_2 and (II) afford *sophorabioside* 5 : 7-Me_2 *ether* (anhyd.), softens at 162°, m.p. 166—168°, (+4H_2O), softens at 130°, m.p. ~140° (slight decomp.), $[\alpha]_D^{20}$ −61·1° in C_5H_5N (hexa-acetate, m.p. 208·5—209° (corr.), $[\alpha]_D^{20}$ −55·6° in C_5H_5N), hydrolysed to (III), which is oxidised by H_2O_2 to *p*-OH·C_6H_4·CO_2H but no *p*-OMe·C_6H_4·CO_2H, (II) is therefore (*A*) but with the side-chain ·C_6H_4·O·$C_6H_{10}O_4$·O·$C_6H_{11}O_4$. H. W.

Neolinarin, a new glucoside from *Linaria vulgaris*, L. G. Zemplén, R. Bognár, and L. Mester (*Ber.*, 1942, **75**, [*B*], 489—495).—Extraction of the foliage and blossoms of the plant with EtOH and purification of the ppt. with C_6H_6 followed by crystallisation from 80% EtOH yields a gelatinous ppt. of pectolinarin (I); the mother-liquors yield *neolinarin* (II) (+2H_2O), m.p. 232—233°, $[\alpha]_D^{18}$ −88·3° in C_5H_5N, −118·5° in AcOH, hydrolysed by acid to pectolinarigenin (III) [6-methoxyacacetin], *d*-glucose, and *l*-rhamnose. Ozonisation of (II) in AcOH leads to rutinose hepta-acetate, m.p. 169—169·5°, $[\alpha]_D^{20}$ −27·7° in $CHCl_3$. HBr in AcOH converts completely acetylated (II) into *monoacetylpectolinarigeninglucoside triacetate* (IV), m.p. 198—199° (corr.), $[\alpha]_D^{22}$ −39·6° in C_5H_5N. (III) and acetobromoglucose give a *pectolinarigeninglucoside tetra-acetate*, m.p. 197·2° (corr.), darkening at 194°, $[\alpha]_D^{17.5}$ −26·2° in $CHCl_3$, converted by Ac_2O and C_5H_5N into *pectolinarigeninglucoside penta-acetate*, m.p. 196° (corr.), softens at 193°, $[\alpha]_D^{25}$ −14·5° in $CHCl_3$, $[\alpha]_D^{23}$ −54·6° in C_6H_6 [also obtained from (IV)], and hydrolysed to *pectolinarigeninglucoside*, m.p. 257—258° (decomp.), $[\alpha]_D^{24}$ −70·0° in C_5H_5N. Very probably (II) is a cryst. form of (I). (II) is transformed into (I) by alkali but the reverse change has not been effected. H. W.

Anhydro-derivative of *D*-mannosan<1, 5>β<1, 6> (presumably 3 : 4-anhydro-*D*-talosan<1, 5>β<1, 6>). R. M. Hann and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 925—928).—2 : 3-*iso*-Propylidene-*D*-mannosan 4-*p*-toluenesulphonate in boiling 20% AcOH gives D-*mannosan*<1, 5>β<1, 6> 4-p-*toluenesulphonate*, m.p. 168°, $[\alpha]_D^{20}$ −80·3° in abs. EtOH (2 : 3-*diacetate*, m.p. 115—116°, $[\alpha]_D^{20}$ −103·4° in $CHCl_3$), which with NaOMe–MeOH at 35° and later room temp. or aq. NaOH at 100° gives 3 : 4-*anhydro*-D-*talosan*<1, 5>β<1, 6>, m.p. 73—74°, $[\alpha]_D^{20}$ −49·5° in H_2O (structure by analogy; 2-p-*toluenesulphonate*, m.p. 147—148°, $[\alpha]_D^{20}$ −19·0° in $CHCl_3$). When this is treated with, successively, Ac_2O–H_2SO_4 at <0° (later 10° and 20°), NaOMe–MeOH–$CHCl_3$, and H_2–Raney Ni in H_2O at 100°/167 atm., it yields *D*-mannitol and *D*-iditol [hexa-acetate (I), m.p. 121—122°, $[\alpha]_D^{20}$ −25·5° in $CHCl_3$]. Crystallographic properties of (I), its *L*- and dl-, m.p. 165—166°, *-isomerides*, and of *D*-mannitol hexa-acetate are described for identification. M.p. are corr. R. S. C.

***X*-Ray diffraction patterns of starches.**—See A., 1942, I, 291.

Starch. XVIII. Fractionation of native starch by dilute alcohol. K. H. Meyer and M. Fuld (*Helv. Chim. Acta*, 1941, **24**, 1408—1409).—The "cryst. amylose" obtained by Wiegel (A., 1942, II, 191) is a mixture of amylose and amylopectin. H. W.

III.—HOMOCYCLIC.

Pro-γ-carotene. L. Zechmeister and W. A. Schroeder (*J. Amer. Chem. Soc.*, 1942, **64**, 1173—1177).—Chromatography of the pigments from the ripe fruit of *Butia capitata* yields *pro-γ-carotene* (I) (0·3 mg. per kg.), m.p. 118—119° (corr.; block; after sintering) (photomicrograph), rubixanthin, neolycopene, a prolycopene, γ-carotene (II) (2 zones), neo-γ-carotene, β-carotene and an isomeride thereof, and 2 unknown pigments. The absorption of (I) (given for 12 solvents) shows max. at 4—6 mμ. < those of (II). 4 or 5 of the ethylenic linkings in (I) are *cis*, the remainder *trans*. Isomerisation of (I) by I or conc. HCl in light petroleum or by heating at 130—135° gives complex mixtures, each component of which, when similarly isomerised, gives a similar mixture. R. S. C.

Quantum-mechanical investigation of the orientation of substituents in aromatic molecules. G. W. Wheland (*J. Amer. Chem. Soc.*, 1942, **64**, 900—908).—Orientation in aromatic mols. is discussed by an essentially mol. orbital method involving consideration of energies of those structures contributing to the activated complex in which a covalent bond is formed between the aromatic ring and the reagent. Substitutions by electrophilic, nucleophilic, and radical reagents can be treated and qual. agreement is obtained. W. R. A.

Alkylation of benzene in presence of acid catalysts. R. L. Burwell, jun., and S. Archer (*J. Amer. Chem. Soc.*, 1942, **64**, 1032—1034).—CHMeEt·OH, α_D^{20} −4·14°, and C_6H_6 in presence of 100% H_3PO_4 at 70°, H_2SO_4 at 53°, or BF_3 at 20° give CHPhMeEt, α_D^{22} +0·055, 0·03°, and 0·065°, respectively. Condensation in presence of H_3PO_4 is as fast as dehydration. Racemisation does not precede reaction since α of CHMeEt·OH is not affected by H_3PO_4. $CHMeEt^+$ is probably an intermediate. BF_3 catalyses condensation of C_6H_6 with *cyclo*hexyl fluoride, but not with the bromide. R. S. C.

Thermal fission of *p*-cymene. H. Breneck and H. F. Müller (*Ber.*, 1942, **75**, [*B*], 554—560).—The chief products of the thermal fission of *p*-$C_6H_4MePr^\beta$ (I) are *p*-C_6H_4Me·CH:CH_2 (II), unchanged (I), PhMe, and products of higher b.p. Under the most favourable conditions (650°; C catalyst and complete absence of metals; use of diminished pressure gives no advantage) the yield of (II) is 54% of the crude (I) obtained from sulphite-cellulose manufacture, or 62·5% of the pure (I) contained therein. Other C_6H_6 derivatives with Pr^β side-chain behave similarly. $PhPr^\beta$ and *iso*thymol give similar yields of styrene derivatives. C has no advantage over other catalysts in the thermal fission of PhEt or C_6H_4MeEt; it appears to have a sp. effect on the elimination of CH_4 from the Pr^β side-chain. H. W.

Influence of hydrogen acceptors on the polymerisation of vinyl derivatives. J. W. Breitenbach and H. L. Breitenbach (*Ber.*, 1942, **75**, [*B*], 505—509).—Diminution of the rate of polymerisation and of the mean chain length of the polymeride is observed as the influence of Bz_2O_2 and chloranil on CHPh:CH_2. The quinone effect is also observed with Me acrylate, methacrylate, and vinyl-acetate. H. W.

Addition polymerisation catalysed by substituted acyl peroxides. C. C. Price, R. W. Kell, and E. Krebs (*J. Amer. Chem. Soc.*, 1942, **64**, 1103—1106).—That catalysis of the polymerisation of CHPh:CH_2 and CH_2:CH·CO_2Me by $(RCO_2)_2$ is due to decomp. to RCO_2· + R· + CO_2 is proved by inclusion of Br, OMe, and Cl in the polymerides (prep., usually, in dioxan) when R = *p*-C_6H_4Br, OMe·C_6H_4, and CH_2Cl, respectively. This accords with the data of Schulz *et al.* (A., 1938, II, 437). *p*-C_6H_4Br·, but not *p*-C_6H_4Br·CO_2·, intervenes in the reaction, since polymerides with CHPh:CH_2 contain only C, H, and Br, and with hot 20% KOH give no *p*-C_6H_4Br·CO_2H. However, the product from $(CH_2Cl·CO_2)_2$ contains O. Prep. of the peroxides (differing for various R) is detailed (cf. Vanino *et al.*, A., 1900, i, 371). R. S. C.

Polymerisation action of dimethyl sulphate. II. Dimerisation of αα-diphenylethylene and the polymerising action of analogues of dimethyl sulphate. V. N. Belov and B. M. Lebedev (*J. Gen. Chem. Russ.*, 1941, **11**, 745—749).—In addition to Me_2SO_4 (A., 1941, II, 284), Et_2SO_4 and *p*-$C_6H_4Me·SO_3Me$ (in order of their activity) cause polymerisation of CPh_2:CH_2, but not $EtNO_3$, $(C_6H_4Me)_3PO_4$, or EtOAc. After short treatment a third dimeride (I) of CPh_2:CH_2, m.p. 200—201°, is isolated (cf. Hughes and Ingold, A., 1933, 262) (yield <4%). Longer treatment causes no increase of (I), but formation of *ααγγ*-tetraphenyl-Δ^α-butene (II), m.p. 113°, further polymerised to 1 : 1 : 3-triphenyl-3-methylhydrindene, m.p. 143°. (I) cannot be further polymerised by heating with Me_2SO_4, does not absorb Br, and is oxidised by CrO_3 to $COPh_2$; it is assumed to be 1 : 1 : 3 : 3-tetraphenyl*cyclo*butane. The polymerising action of Me_2SO_4 is due to its decomp. products, probably $MeHSO_4$. G. A. R. K.

Preparation of ααβ-triphenylethane. P. Bert (*Compt. rend.*, 1941, **213**, 792—793).—C_6H_6 (10 mols.), $CH_2Cl·CHCl_2$ (I) (1 mol.), and $AlCl_3$ (10 g.) at 100° yield 80% of $CHPh_2·CH_2Ph$ (II), b.p. 211°/14 mm., accompanied by CH_2Ph_2 and (CHPh:)$_2$ due to formation of CH_2Cl_2 and (CHCl:)$_2$ from (I). C_6H_6 and (CHCl:)$_2$ also afford (II). C. S.

Substituted diphenylbutadienes. I. Addition of bromine to α-phenyl-δ-*p*-bromophenyl-$\Delta^{\alpha\gamma}$-butadiene. K. A. Huggins and O. E. Yokley (*J. Amer. Chem. Soc.*, 1942, **64**, 1160—1161).—*p*-$C_6H_4Br·CH_2·CO_2H$, CHPh:CH·CO_2H, Ac_2O, and PbO give *α-phenyl-δ-p-bromophenyl-*$\Delta^{\alpha\gamma}$*-butadiene* (I) (18·4%), m.p. 163° [(:CH·CO)$_2$O *adduct*, m.p. 226°]. With Br in $CHCl_3$ at 0° (I) gives *αβγδ-tetrabromo-α-phenyl-δ-p-bromophenyl-n-butane*, m.p. 230°, or with 1 mol. at 0° or <0° in accordance with Ingold's theory (A., 1931, 1207), only *γδ-dibromo-δ-phenyl-α-p-bromophenyl-*Δ^α*-n-butene*, m.p. 129—130°, oxidised by O_3 in $CHCl_3$ or $KMnO_4$–$MgSO_4$–$COMe_2$ to CHPhBr·CHBr·CO_2H (64·8%) and *p*-$C_6H_4Br·CHO$ (62·26%). R. S. C.

Attempted synthetic preparation of the antirachitic vitamins. X. New path to the synthesis of the unsaturated system. K. Dimroth and E. Stockstrom (*Ber.*, 1942, **75**, [*B*], 582—586).—2-Dimethylaminomethyl*cyclo*hexyl chloride is converted by successive treatment with Mg and 1-decahydronaphthylideneacetaldehyde into α-2-dimethylaminomethyl*cyclo*hexyl-β-1′-decahydronaphthylideneethyl alcohol, which is degraded (Hofmann) to 2-methylenedeca-

hydronaphthylidene-ethylidene*cyclo*hexane [adduct with $(CH\cdot CO)_2O$, m.p. 180—181°]. H. W.

Diterpenes. XLIX. Synthesis of 1-methyl-7-ethylphenanthrene and of 1-methyl-7-*sec.*-butylphenanthrene. β-Ethylretene. L. Ruzicka and S. Kaufmann [with M. Hinder, J. Pataki, G. Sagen, T. Grauer, W. Janett, R. Tanner, H. Simon, L. Werner, and T. Suter] (*Helv. Chim. Acta*, 1941, **24**, 939—945).—2-$C_{10}H_7Et$, $(CH_2\cdot CO)_2O$, and $AlCl_3$ give *γ-keto-γ-6-ethyl-2-naphthylbutyric acid*, m.p. 170—171°, the *Me* ester, m.p. 69·5°, of which is transformed by MgMeI followed by hydrolysis into *γ-6-ethyl-2-naphthyl-Δ$^{\beta}$-pentenoic acid*, m.p. 135—137°, reduced to the *-valeric acid*, m.p. 120°. This is converted by P_4O_{10} in dry C_6H_6 into *4-keto-1-methyl-7-ethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene* [additive *compound*, m.p. 99—100°, with $C_6H_3(NO_2)_3$], transformed (Wolff–Kishner) and dehydrogenated (Pd–C at 300°) to *1-methyl-7-ethylphenanthrene*, m.p. 87·5° [additive *compound*, m.p. 134°, with $C_6H_3(NO_2)_3$]. 2-$C_{10}H_7Ac$ and MgEtI afford *2-sec.-butenylnaphthalene*, b.p. 153—154°/13 mm., hydrogenated (Raney Ni) to *2-sec.-butylnaphthalene*, b.p. 138—139°/14·5 mm. This gives successively *γ-keto-γ-6-sec.-butylnaphthylbutyric acid*, m.p. 130—130·5°, its *Me* ester, m.p. 58·5—59°, *γ-6-sec.-butyl-2-naphthyl-Δ$^{\beta}$-pentenoic acid*, m.p. 113°, *γ-6-sec.-butyl-2-naphthylvaleric acid*, m.p. 91·5°, *4-keto-1-methyl-7-sec.-butyl-1 : 2 : 3 : 4-tetrahydrophenanthrene* [additive *compound*, m.p. 76·5—77·5°, with $C_6H_3(NO_2)_3$], *1-methyl-7-sec.-butyl-1 : 2 : 3 : 4-tetrahydrophenanthrene*, a liquid [additive *compound*, m.p. 57—60°, with $C_6H_3(NO_2)_3$], and *1-methyl-7-sec.-butylphenanthrene*, m.p. 62·5—63° [additive *compound*, m.p. 132—133°, with $C_6H_3(NO_2)_3$]. β-Ethyldihydroretene is dehydrogenated by Pd–C at 320° to β-ethylretene, m.p. 91—93° [additive *compound*, m.p. 153—154° with $C_6H_3(NO_2)_3$; corresponding *quinoxaline* derivative, m.p. 133—134°]. M.p. are corr. H. W.

Optically active vasopressor amines. W. R. Brode and M. S. Raasch (*J. Amer. Chem. Soc.*, 1942, **64**, 1449—1450).—$CHPhMe\cdot CH_2\cdot NH_2$ with *l*-malic acid in EtOH and from the mother-liquors by the *d*-acid gives the *d*-base *l*-malate and *l*-base *d*-malate, m.p. 182—184°, $[\alpha]_D^{22-26}$ ±21·9° in H_2O; resolution by *d*-tartaric acid is slow, giving the d-*base* (10—15%), b.p. 102°/2 mm., $[\alpha]_D^{29}$ +35·4° in EtOH; resolution by camphorsulphonic (**I**) or menthoxyacetic acid is very slow. $CHPhMe\cdot CH_2\cdot NHMe$ with *d*-(**I**) in EtOAc and from the mother-liquors by *d*-mandelic acid in EtOH–Et_2O gives the d-, b.p. 103°/21 mm., $[\alpha]_D^{23}$ +32·2° in EtOH (*d*-camphorsulphonate, m.p. 118—119°, $[\alpha]_D^{25}$ +28·8° in H_2O), and l-*amine*, b.p. 101—102°/19 mm., $[\alpha]_D^{22}$ −31·7° in EtOH (*d*-mandelate, m.p. 86—87°, $[\alpha]_D^{22}$ +39·8°), respectively. R. S. C.

Action of potassium hypobromite on β-phenyl-αα-dimethylpropionamide. C. Mentzer (*Compt. rend.*, 1941, **213**, 581—584).—$CH_2Ph\cdot CMe_2\cdot CO\cdot NH_2$ and cold aq. KOBr give *β-phenyl-αα-dimethylethylcarbimide* (**I**), b.p. 112—115°/20 mm., 225°/760 mm.; at 60° *s-di-(β-phenyl-αα-dimethylethyl)carbamide*, m.p. 184—185° [with $Ca(OH)_2$ at 230° affords *β-phenyl-αα-dimethylethylamine* (**II**), b.p. 203—205°/760 mm.], results. PhNCO and (**II**) or NH_2Ph and (**I**) give *N-phenyl-N′-β-phenyl-αα-dimethylethylcarbamide*, m.p. 150—151°. W. C. J. R.

Colour reactions of sympathomimetic amines with diazonium compounds. K. H. Beyer (*J. Amer. Chem. Soc.*, 1942, **64**, 1318—1322).—Sympathomimetic aralkylamines are coupled with *p*-$NO_2\cdot C_6H_4\cdot N_2Cl$ (**I**) (M./1600) at 21°, treated after 1 hr. slowly with 1·1% Na_2CO_3 and 10 min. later with 10% NaOH, and extracted with $Bu^{\alpha}OH$; the colour in the $Bu^{\alpha}OH$ is then measured. (*A*) Primary amines having no phenolic OH (12 examples) give a red colour, the reactions being: NH_2R + (**I**) → $NHR\cdot HCl\cdot N:N\cdot C_6H_4\cdot NO_2$ → $NHR\cdot N:N\cdot C_6H_4\cdot NO_2$ ⟷ (Na_2CO_3) $NR:N\cdot NH\cdot C_6H_4\cdot NO_2$ ⟷ $NR:N\cdot N:C_6H_4:NO\cdot OH$ (pale yellow) ⟷ (NaOH) $NR:N\cdot N:C_6H_4:NO\cdot ONa$-*p* (red). Evidence for these reactions is: (i) immediate addition of NaOH (to give p_H ~11) prevents colour formation; (ii) migration of H and development of colour is prevented by use of *sec.* or *tert.* amines; (iii) the NO_2 is essential since *p*-$SO_3H\cdot C_6H_4\cdot N_2Cl$ or *p*-$C_6H_4Me\cdot N_2Cl$ (**II**) gives no colour; (iv) quinonoid structure is essential since (**II**), *m*-$NO_2\cdot C_6H_4\cdot N_2Cl$ (**III**), and 4 : 2 : 1-$NO_2\cdot C_6H_3Cl\cdot N_2Cl$ (**IV**) give no colour; and (v) the final step is reversible by HCl–NaOH. Absorption spectra (detailed) have absorption max. at 525 ± 5 mμ., but the mol. extinction coeff. varies from ~200 to ~1250. (*B*) Amines having one phenolic OH (9 examples) give red colours, the reactions being: → 1 : 4 : 2-$OH\cdot C_6H_3X\cdot N:N\cdot C_6H_4\cdot NO_2$ (X = side-chain carrying the N) → (Na_2CO_3) 1 : 4 : 2-$O\cdot C_6H_3X:N\cdot NH\cdot C_6H_4\cdot NO_2$ → 1 : 4 : 2-$O\cdot C_6H_3X:N\cdot N:C_6H_4:NO\cdot OH$-*p* ⇌ 1:4:2-$O\cdot C_6H_3X:N\cdot N:C_6H_4:NO\cdot ONa$-*p* (red). Evidence is: (i) reaction is not at the N since *sec.* amines give the colour [cf. class (*A*)]; (ii) the *o*-quinonoid structure may be the reason why ε is > in class (*A*) but is not the sole cause of colour since (**IV**) gives only a very faint colour; (iii) the *p*-NO_2 is involved since (**III**) gives an orange, and (**II**) a yellow, colour. OH (or α-CO) in the side-chain inhibits the reactivity of the phenolic OH but decreases the intensity of sp. absorption bands (also lower for *sec.* amines). (*C*) Pyrocatechol derivatives (4 examples) give green colours, reactions being probably as above but leading to 1 : 5 : 2 : 4-$O\cdot C_6H_2X(OH):N\cdot N:C_6H_4:NO\cdot ONa$-*p* (absorption max. at 640 ± 5 mμ.). If the side-chain is omitted, the colour is yellow and divided between the alkaline and BuOH layers; Me as side-chain deepens the colour and increases its solubility in BuOH. Other details are also discussed. R. S. C.

Regularities in the hydrogenative fission of *N*-benzyl compounds. L. Birkofer (*Ber.*, 1942, **72**, [*B*], 429—441).—$CH_2Ph\cdot NH_2$, $NH(CH_2Ph)_2$, and NHAlk·CH_2Ph are unaffected by H_2 in presence of PdO. $N(CH_2Ph)_3$ in AcOH and $N(CH_2Ph)_3$,HCl in H_2O give $NH(CH_2Ph)_2$. Benzylmethyl-laurylamine and -cetylamine are converted into methyl-laurylamine and -cetylamine, respectively. Dibenzyldodecylamine is hydrogenated (PtO_2 in AcOH) to hexahydrobenzyldodecylamine (*hydrochloride*, m.p. 218°). $NH_2\cdot N(CH_2Ph)_2$ yields (H_2, PdO, EtOH) $NH_2\cdot NH\cdot CH_2Ph$, whilst $[N\cdot N(CH_2Ph)_2]_2$ gives $NH(CH_2Ph)_2$. $N(CH_2Ph)_3Me\cdot OH$ readily affords $CH_2Ph\cdot NHMe$ (*flavianate*, m.p. 190°; *picrolonate*, m.p. 210°) whereas $N(CH_2Ph)_3MeI$ is not reduced. $NPh(CH_2Ph)Me_2Cl$ yields *cyclo*hexyldimethylamine. 2-Benzyldihydro*iso*indole gives dihydro*iso*indole. 1 : 4-Dibenzylpiperazine loses 2 mols. of PhMe and 5-amino-1-benzyl-1 : 2 : 3 : 4-tetrazole is hydrogenated to aminotetrazole. 2 : 4 : 6-*Tri-imino*-1 : 3 : 5-*tribenzyl*-1 : 3 : 5-*triazine* (**I**), m.p. 129—130° (obtained by addition of Br in EtOAc to $CH_2Ph\cdot NH_2$ and KCN in aq. EtOAc and treatment of the product with NaOH), gives melamine. Elimination of CH_2Ph from 2-imino-1-benzyl-1 : 2-dihydropyridine is slow and incomplete and accompanied by nuclear hydrogenation, the products being 2-amino-3 : 4 : 5 : 6-tetrahydropyridine and 2-imino-1-benzylpiperidine (*picrate*, m.p. 106°). 2-Benzylaminopyridine does not lose CH_2Ph but is hydrogenated to 2-*benzylamino*-3 : 4 : 5 : 6-*tetrahydropyridine*, m.p. 40—41° (*picrate*, m.p. 131°; *picrolonate*, m.p. 199°). Aromatic rings, CO_2H, and CN activate so that CH_2Ph is removed from *sec.* N. $NHPh\cdot CH_2Ph$ gives quantitatively (PdO) NH_2Ph and PhMe or (PtO_2) mainly *cyclo*hexylhexahydrobenzylamine with minor quantities of *cyclo*hexylamine and hexahydrotoluene. $NPh(CH_2Ph)_2$ yields NH_2Ph and PhMe whilst 2-*dibenzylaminonaphthalene*, m.p. 119°, affords β-$C_{10}H_7\cdot NH_2$ and PhMe. *Dibenzylglycine*, m.p. 200°, and its *Me* ester, m.p. 41°, afford glycine and $NH_2\cdot CH_2\cdot CO_2Me$, respectively. $CN\cdot N(CH_2Ph)_2$ yields $CN\cdot NH_2$ or (**I**) owing to polymerisation of $CN\cdot NH\cdot CH_2Ph$ if hydrogenation is interrupted before it is complete. $(CO\cdot NH\cdot CH_2Ph)_2$ and *NN-dibenzylurethane*, b.p. 169°/2 mm., are stable towards H_2. H. W.

Catalytic activity of an intermetallic compound of cadmium and copper in the vapour-phase reduction of nitrobenzene.—See A., 1942, I, 333.

Nitroamines. IX. Formation of nitroamines and their conversion into nitroanilines. E. Macciotta (*Gazzetta*, 1941, **71**, 81—94).—*o*- and *p*-$NO_2\cdot C_6H_4\cdot NH_2$ in AcOH with HNO_3 (*d* 1·52) and Ac_2O give *o*- (**I**) and *p*-$NO_2\cdot C_6H_4\cdot NH\cdot NO_2$ (**II**), respectively. In conc. H_2SO_4, (**I**) gives 2 : 4 : 1- (**III**) and 2 : 6 : 1-$(NO_2)_2C_6H_3\cdot NH_2$; (**II**) gives (**III**). Similarly 2 : 3 : 1-$(NO_2)_2C_6H_3\cdot NH\cdot NO_2$ gives 2 : 3 : 6- (**IV**), m.p. 234° (? 134°) (80%), and 2 : 3 : 4-*trinitroaniline* (**V**), m.p. 210° (20%). With 20% NaOH and MeOH, (**IV**) gives the *Me ether*, m.p. 177—178°, of 2 : 4-dinitro-3-aminophenol, m.p. 202°, obtained from (**IV**) and $Ba(OH)_2$–MeOH. In conc. H_2SO_4, the Ag salt of 2 : 5 : 1-$(NO_2)_2C_6H_3\cdot NH\cdot NO_2$ gives (**IV**) (70%) and 2 : 4 : 5-*trinitroaniline* (**VI**), m.p. 202° (30%), which with $Ba(OH)_2$–MeOH gives 4 : 6-dinitro-3-aminophenol, m.p. 225°. Similarly the Hg salt of 3 : 4 : 1-$(NO_2)_2C_6H_3\cdot NH\cdot NO_2$ gives (**VI**) (70%) and (**V**) (30%). The results are discussed in relation to the Koerner structure for C_6H_6, and to electronic theories of substitution. E. W. W.

Amino-alcohols. X. Intermediates of pentryl analogues. Chloronitroanilinoalkanols. C. B. Kremer and M. Meltsner (*J. Amer. Chem. Soc.*, 1942, **64**, 1285—1286; cf. A., 1940, II, 276).—The appropriate $C_6H_3Cl_2\cdot NO_2$ and amine in boiling $Bu^{\alpha}OH$ give β-4-*chloro-2-nitroanilino-ethyl*, m.p. 107·5°, -iso*propyl*, m.p. 116·5°, -tert.-, m.p. 121·5°, and -iso-*butyl*, m.p. 122°, *γ-4-chloro-2-nitroanilino-n-propyl*, m.p. 60°, *β-2-chloro-4-nitroanilino-ethyl*, m.p. 120°, -iso*propyl*, m.p. 144°, and -tert.-*butyl*, m.p. 71·5°, *γ-2-chloro-4-nitroanilino-n-propyl*, m.p. 73°, *β-5-chloro-2-nitroanilino-ethyl*, m.p. 116°, -iso*propyl*, m.p. 109°, and -tert.-*butyl*, m.p. 127°, *γ-5-chloro-2-nitroanilino-n-propyl*, m.p. 78·5°, *β-3-chloro-2-nitroanilino-ethyl*, m.p. 78·5°, -iso*propyl*, m.p. 83·5°, and -tert.-*butyl*, m.p. 98·5°, and *β-6-chloro-2-nitroanilinoethyl*, b.p. 155—157°/2 mm., *alcohol*. Thence $Na_2S_2O_4$ in weak aq. alkali yields *β-4-chloro-2-aminoanilino-ethyl*, m.p. 122·5°, -iso*propyl*, m.p. 130°, -tert.-, m.p. 121°, and -iso-*butyl*, *β-5-chloro-2-aminoanilino-ethyl*, m.p. 104·5°, and -iso*propyl*, m.p. 101·5°, *γ-5-chloro-2-aminoanilino-n-propyl*, m.p. 73·5°, *β-3-*, m.p. 74°, and *β-6-chloro-2-aminoanilinoethyl*, b.p. 135—137°/2 mm., *alcohol*. R. S. C.

Restricted rotation in arylamines. III. Preparation and resolution of 1-*N*-methyl-β-carboxypropionamido-2-methylnaphthalene and -4-chloro-2-methylnaphthalene. R. Adams and A. A. Albert (*J. Amer. Chem. Soc.*, 1942, **64**, 1475—1478; cf. A., 1942, II, 138).—The *peri*-CH of a $C_{10}H_8$ ring offers less interference than does Me in a C_6H_6 ring. 2 : 1-$C_{10}H_6Me\cdot NH_2$ (**I**) (prep. from the NO_2-compound by H_2–Raney Ni in EtOH at room temp./1—3 atm.) with Me_2SO_4–H_2O and then $OH\cdot CHPh\cdot SO_3Na$ gives *1-methylamino-2-methylnaphthalene* (81%), b.p. 106—108°/2 mm., the *β-carboxypropionyl* derivative

[prep. by $(CH_2{\cdot}CO)_2O$ and a drop of H_2SO_4 in C_6H_6], m.p. 109°, of which is resolved by quinine in EtOAc to l-, m.p. 108° (*quinine* salt, +0·5EtOAc, m.p. 129·5°, $[\alpha]_D^{27}$ −128°), and d-*forms*, m.p. 107—108° (quinine salt, m.p. 99—100°, $[\alpha]_D^{27}$ −57°), $[\alpha]_D^{27}$ −75°, +74°, which in boiling $Bu^{\alpha}OH$ have a half-life period 5·7 hr. 2 : 4 : 1-$C_{10}H_5McCl{\cdot}NH_2$ gives similarly 4-*chloro*-1-*methylamino*-2-*methylnaphthalene*, m.p. 30°, b.p. 136—137°/0·5 mm., and its dl-, m.p. 167·5—168·5°, d-, m.p. 115·5—116°, $[\alpha]_D^{30}$ +56° (*quinine* salt, +0·5EtOAc, m.p. 117—119°, $[\alpha]_D^{30}$ −56°), and impure l-*β-carboxypropionyl* derivative, softens at 116°, m.p. up to 163—167°, $[\alpha]_D^{20}$ −36°; the half-life period in boiling $Bu^{\alpha}OH$ is 4·1 hr. (**I**) gives similarly 1-*ethylamino*-2-*methylnaphthalene*, m.p. 108—109°/0·3 mm., but the *β-carboxypropionyl* derivative, m.p. 123°, thereof could not be resolved. M.p. are corr. [α] are in EtOH. R. S. C.

Sulphonating action of dialkyl sulphates. I. Interaction of dimethyl sulphate with diphenylmethyl- and triphenyl-amine. V. N. Belov (*J. Gen. Chem. Russ.*, 1941, **11**, 750—756).—NPh_2Me heated with Me_2SO_4 yields, in addition to the quaternary salt, Me_2O and sulphonation products of NPh_2Me. NPh_3 and Me_2SO_4 at 150° form no quaternary salt, but give Me_2O, MeOH, and sulphonation products of NPh_3. The formation of sulphonation products is attributed to $MeHSO_4$ formed by hydrolysis of Me_2SO_4 by traces of moisture. A similar process may account for the isolation of Me_2O during the methylation of certain brucidine derivatives (A., 1935, 1389). G. A. R. K.

Chemotherapeutic pyroplasmocidal compounds. I. Dialkylaminophenylcarbamides. M. P. Gertschuk (*J. Gen. Chem. Russ.*, 1941, **11**, 731—738).—(*p*-$NAlk_2{\cdot}C_6H_4{\cdot}NH)_2CO$ have been prepared in the hope of improving on the chemotherapeutic properties of akaprin (pyroplasmin) (**I**); one of them, the hydrochloride of (**III**) (below), is effective in cattle infected with *Babasiella bovis* and its M.T.D. is 10—20 times that of (**I**). *p*-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$ (**II**) and $CO(NH_2)_2$ at 148° afford (*p*-$NMe_2{\cdot}C_6H_4{\cdot}NH)_2CO$ (**III**), m.p. 253—255° (*dihydrochloride*, m.p. 242°; *dimethosulphate*, m.p. 215°). (**II**) and *p*-$NMe_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO_2Et$ give a base, m.p. 253°. *p*-$NH_2{\cdot}C_6H_4{\cdot}NEt_2$ and $CO(NH_2)_2$ give (*p*-$NEt_2{\cdot}C_6H_4{\cdot}NH)_2CO$, m.p. 218—220° (cf. Zetzsche and Nerger, *Ber.*, 1940, **73**, [*B*], 476) (*dihydrochloride*, m.p. 240—241°). The *p*-NO-derivative of $NPhPr_2$ (improved prep.) is reduced by Zn and HCl to *p*-$NH_2{\cdot}C_6H_4{\cdot}NPr_2$, which with $CO(NH_2)_2$ in PhOH gives NN′-*di*-p-*dipropylaminophenylcarbamide*, m.p. 186° (*dihydrochloride*, m.p. 224—225°; *dimethosulphate*, m.p. 233°). (**III**) affords a $(NO_2)_2$-compound, m.p. 188—189°. The *methosulphate* of *p*-$NMe_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NHPh$ has m.p. 177—178°. G. A. R. K.

Long-chain sulphonamides and their therapeutic properties. H. Arnold, E. Helmert, T. Möbus, R. Prigge, H. Rauen, and T. Wagner-Jauregg (*Ber.*, 1942, **75**, [*B*], 369—378).—*Na hydnocarpylsulphonate*, decomp. 150—155°, shrinks at 135°, *hydnocarpylsulphonamide* (**I**), m.p. 90—92°, N⁴-*undecenoyl*- (**II**), m.p. 196—198°, N⁴-*chaulmoogroyl*- (**III**), m.p. 185—187° after softening, N⁴-*dodecoyl*- (**IV**), m.p. 207—208°, N^1-dodecoyl- (**V**), m.p. 113—114° (lit. 120—122°), N⁴-acetyl-N^1-oleyl-, m.p. 126—127° (lit. 131—135°), N^1-oleyl- (**VI**), m.p. 120°, N⁴-*acetyl*-N¹N⁴-*dioleyl*-, m.p. 92°, and N¹-*hydnocarpyl*- (**VII**), m.p. 116°, -*sulphanilamide*, and *Na* N¹-*oleylsulphanilamidoformaldehyde H sulphite* are described. Towards pneumococcus infection (**III**) and N^4-undecoylsulphanilamide (**VIII**) are inactive, (**II**) is possibly somewhat active, (**IV**) as potent as the unsubstituted material, whereas (**V**) is less active. 2-Aminobenzthiazole-6-sulphonamide and its 6-Ac derivative have little therapeutic action towards pneumococcus infection whereas 2-dodecoamido- and 2-chaulmoogroylamido-benzthiazole-6-sulphonamide are noticeably active, possibly owing to better tolerance. Sulphapyridine and (**V**) are ineffective against tuberculosis in guinea-pigs, and (**IV**), (**V**), and (**VIII**) and lauroylsulphapyridine are without action towards leprosy in rats, as are also (**VI**) and (**VII**), whereas (**I**) is slightly active. H. W.

Sulphonamides. J. C. Somaglino (*Rev. Fac. Cienc. Quím., La Plata*, 1941, **16**, 227—234).—4′-Nitro- was reduced (Sn, HCl) to 4′-*amino-diphenyl*-4-*sulphonamide*, m.p. 262—263° ·(decomp.). *p*-$NO_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}SO_2Cl$-*p* with NH_2Ph yields 4′-*nitro*-, m.p. 182—183°, reduced (Sn, HCl) to 4′-*amino-diphenyl*-4-*sulphonanilide*, m.p. 182—183°. *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$, *p*-$C_6H_4Ph{\cdot}NH_2$, and C_5H_5N in $COMe_2$ give the *Ac* derivative, m.p. 169°, of 4-*sulphanilamidodiphenyl*, m.p. 247°. The *Ac* derivative, m.p. 245°, of 2-*sulphanilamidofluorene*, m.p. 239°, was prepared similarly. F. R. G.

NN′-**Diacetylsulphanilyl- and** *NN′*-**disulphanilyl-***l*-**cystine.** F. Irreverre and M. X. Sullivan (*J. Amer. Chem. Soc.*, 1942, **64**, 1488—1489).—*l*-Cystine and *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ in aq. NaOH give NN′-*di*-N⁴-*acetylsulphanilyl*-, m.p. 204—206° (decomp.), and thence (hot 10% HCl) NN′-*disulphanilyl*-l-*cystine*, m.p. 193—194° (decomp.). R. S. C.

Sulphonamide [derivatives]. III. *N*-**Substituted derivatives.** N. Giovambattista (*Rev. Fac. Cienc. Quím., La Plata*, 1941, **16**, 217—226; cf. Novelli *et al.*, A., 1941, II, 165).—$CH_2(C_6H_4{\cdot}NH_2$-*p*$)_2$, *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$, and C_5H_5N in $COMe_2$ yield the Ac_2 derivative (+$2H_2O$), m.p. 243·5—245°, of 4 : 4′-*disulphanilamidodiphenylmethane*, m.p. 219·5—220·5°. 4 : 4′-*Disulphanilamidodiphenylsulphone* (+1·5C_6H_6), translucent at 136°, melting commences at 141—142°, is prepared by hydrolysis (aq. NaOH) of its Ac_2 derivative, new m.p. 292—293°. Similarly prepared were 4-*nitro*-4′-*sulphanilamidodiphenylsulphone*, m.p. 191—192° (*Ac* derivative, m.p. 279—280°), and *sulphoxide*, m.p. 238—239° (decomp.) [*Ac* derivative, m.p. 263—264·5° (decomp.)]. F. R. G.

p-**Acylamidobenzenesulphonhydroxylamides.**—See B., 1942, III, 203.

Polysulphanilamido-compounds.—See B., 1942, III, 203.

Reactions of diazonium salts of arylazo-β-naphthylamines. H. H. Hodgson and C. K. Foster (*J.C.S.*, 1942, 435—437).—Solid 1 : 2-NAr·N·$C_{10}H_6{\cdot}N_2X$ (**I**) are obtained (exceptions noted) from the amine (*A*) by addition of solid $NaNO_2$ to (*A*) in AcOH–HCl (*d* 1·16; limited amount) or by use of AcOH–$NO{\cdot}SO_4H$ (alternative procedures). (**I**) readily afford the corresponding naphthols with a very small amount of H_2O (*e.g.*, during prep.; action of EtOH), with AcOH–Br give diazo-perbromides (when heated yield N_2 and Br-derivatives), do not couple with phenols, and do not afford hydrazines with $SnCl_2$–HCl. 2-*Bromo*-1-2′ : 5′-*dichloro*-, m.p. 138°, and -1-m-*chloro-benzeneazonaphthalene*, m.p. 123°, are described. The compound, m.p. 204°, obtained by Zincke *et al.* (A., 1888, 159) by reduction of (**I**) (Ar = Ph, X = HSO_4) is formulated as $C_{10}H_6\langle^{N(NHPh)}_{NH}\rangle NH$; an analogous *compound*, $C_{16}H_{13}N_4Cl$, m.p. 196°, decomp. 197°, is formed from (**I**) (Ar = *o*-C_6H_4Cl, X = HSO_4) and $SnCl_2$–HCl. C. S.

Reactions between *s*-**diphenyltriazen and mercuric salts.** C. M. Knowles and G. W. Watt (*J. Amer. Chem. Soc.*, 1942, **64**, 935—937).—Contrary to Mandal (*Sci. & Cult.*, 1940, **6**, 59), NHPh·N:NPh (**I**) with $HgCl_2$ or $HgBr_2$ in EtOH gives *compounds*, 2(**I**),$HgCl_2$, m.p. 161—165° (decomp.), and 2(**I**),$HgBr_2$, m.p. 132—134° (decomp.), respectively, with $Hg(OAc)_2$–EtOH gives the yellow salt (**II**) $Hg(NPh{\cdot}N{\cdot}NPh)_2$, m.p. 232° (decomp.; rapid heating) or 227° (decomp.; slow heating), and with $Hg(NO_3)_2$ gives, according to the conditions, (**II**), a red, m.p. 212° (decomp.) or (+$2C_5H_5N$) 216° (decomp.), or orange *isomeride*, m.p. 187° (decomp.), or substances of lower N content. M.p. are corr. R. S. C.

Nuclear methylation of phenols.—See B., 1942, II, 313.

Soluble derivatives of chlorocresol. W. H. Linnell (*Quart. J. Pharm.*, 1942, **15**, 111—118).—6-Chloro-4-amino-*m*-cresol (**I**) (prep. described) with PhCHO yields the :*CHPh* derivative, m.p. 128—129°, which does not form a stable compound with H_2SO_3 or $NaHSO_3$. The *cinnamylidene* derivative, m.p. 124·5—126°, of (**I**) combines with H_2SO_3; the product is isolated first as *Ba* and then *Na*$_2$ 6-*chloro*-4-(*αγ-disulpho-γ-phenylpropylamino*)-m-*cresol*. It is not bactericidal. J. N. A.

Production of cresols and higher phenols by fusion.—See B., 1942, II, 313.

Coupling of *m*-**halogenophenols with diazotised aniline and existence of chromoisomerism among 3-halogeno-4-benzeneazophenols.** H. H. Hodgson and G. Turner (*J.C.S.*, 1942, 433—435; cf. A., 1942, II, 9).—PhN_2Cl and *m*-$C_6H_4Cl{\cdot}OH$ couple in aq. Na_2CO_3 (not NaOAc) to 3-chloro-4-benzeneazophenol, forms, m.p. 95°, 104°, and 114°, and in aq. NaOH (even with equimol. quantities) to 3-chloro-2 : 4-bisbenzenazophenol (**I**), m.p. 181° (no trisazo-derivative formed). *m*-$C_6H_4Br{\cdot}OH$ affords similarly and respectively 3-*bromo*-4-*benzeneazophenol*, forms, m.p. 128° and 161—163°, and 3-*bromo*-2 : 4-*bisbenzeneazophenol* (**II**), m.p. 175°, whilst *m*-$C_6H_4I{\cdot}OH$ gives 3-*iodo*-4-*benzeneazophenol*, forms, m.p. 138° and 145°, and 3-*iodo*-2 : 4-*bisbenzeneazophenol* (**III**), m.p. 187°. The above forms are chromoisomerides; they are reduced to 4 : 3 : 1-$NH_2{\cdot}C_6H_3Hal{\cdot}OH$ and thence oxidised to 2-halogenobenzoquinones. (**II**) and (**III**), but not (**I**), with boiling aq. KOH give 2 : 4-bisbenzeneazoresorcinol. (**I**) with $Na_2S_2O_4$ yields 3-*chloro*-2 : 4-*diaminophenol*, m.p. 200° (*Bz*$_2$ derivative m.p. 192°), converted ($NO{\cdot}SO_4H$ in AcOH, then CuCl) into 2 : 3 : 4 : 1-$C_6H_2Cl_3{\cdot}OH$. 4 : 6 : 3 : 1-$(NO_2)_2C_6H_2Cl{\cdot}OH$ is reduced (Zn–HCl) to 4 : 6 : 3 : 1-$(NH_2)_2C_6H_2Cl{\cdot}OH$ (*Bz*$_2$ derivative, m.p. 215°). C. S.

Vicinal substituted resorcinols. II. Alkylresorcinols. Synthesis of γ-*n*-**hexyl-,** γ-*n*-**heptyl-, and** γ-*n*-**octyl-resorcinol.** A. Russell and H. C. Gulledge (*J. Amer. Chem. Soc.*, 1942, **64**, 1313—1315; cf. A., 1940, II, 304).—2 : 6 : 1-$(OMe)_2C_6H_3{\cdot}CN$ (**I**) and MgRCl in Et_2O and later boiling PhMe (N_2) give 2-n-*hexoyl*- (70%), b.p. 142°/2 mm., -*heptoyl*- (83·2%), b.p. 160—164°/2 mm., and -*octoyl-resorcinol Me*$_2$ *ether* (57%), b.p. 163—165°/1·5 mm., converted by $AlCl_3$ in PhMe at >120° (bath) into 2-n-*hexoyl*- (64·8%), m.p. 74°, -*heptoyl*- (71%), m.p. 75°, and -*octoyl-resorcinol* (61·5%), m.p. 78°, which are reduced by Zn–Hg–HCl–AcOH–H_2O to 2-n-*hexyl*- (42·9%), m.p. 67°, -*heptyl*- (49%), m.p. 51—52°, and -*octyl-resorcinol* (63%), m.p. 55—56° (no $FeCl_3$ colours). *n*-$C_{12}H_{25}{\cdot}MgBr$ and (**I**) give only *n*-$C_{24}H_{50}$ (21%). R. S. C.

Reduction of dipole moment by steric hindrance in di-*tert.***-butylquinol and its dimethyl ether.**—See A., 1942, I, 289.

Halogenation of phenolic ethers and anilides. Arrhenius activation energies.—See A., 1942, I, 332.

Synthesis of engenol. L. J. Briusova and M. L. Joffe (*J. Gen. Chem. Russ.*, 1941, **11**, 722—728).—Guaiacol allyl ether (I) with BF_3 in kerosene solution, or with BF_3,2AcOH without a solvent, affords 20—22% of eugenol, 10—15% of guaiacol, and 30% of unchanged (I). Possible by-products are allyleugenol, its allyl ether, and allylguaiacol allyl ether. G. A. R. K.

Fission of phenolic ethers by pyridine hydrochloride. II. V. Prey (*Ber.*, 1942, **75**, [*B*], 350—356).—PhOMe and C_5H_5N,HCl (I) are heated at 220° and periodical determinations are made of (I) acidimetrically, total Cl argentometrically, and PhOMe gravimetrically. After 2 hr. no PhOMe remains and there is no further consumption of (I). Total Cl is little changed, indicating that liberated MeCl is completely retained and suggesting the existence of an additive compound of (I) and PhOMe. C_5H_5NMeCl and dry HCl at 220° give almost quantitatively MeCl and C_5H_5N,2HCl (II), later $(C_5H_5N)_2$,3HCl (III). Complete fission of ethers, except PhOMe, is caused by dry HCl + 20% of (I) at 200°. Apparently PhOMe is affected only by (I) whereas guaiacol (IV) etc. is acted on by added HCl and thus by (II) or (III). Veratrole, nerolin, and (IV) are completely hydrolysed by HCl and 10% of C_5H_5N at 210° and reaction can be effected slowly with (IV) in presence of 1% of C_5H_5N. H. W.

Sulphonating action of dialkyl sulphates. II. Interaction of dimethyl sulphate with ethers. V. N. Belov and E. I. Schepelenkova (*J. Gen. Chem. Russ.*, 1941, **11**, 757—762).—Me_2SO_4 heated with phenolic ethers gives sulphonic acids and Me_2O. Thus, PhOMe affords *p*-OMe·C_6H_4·SO_3H (40%) and its Me ester (27%) (cf. A., 1923, i, 462); Ph_2O gives *p*-OPh·C_6H_4·SO_3H (69%) and its Me ester (22%); β-$C_{10}H_7$·OMe affords 2 : 6-OMe·$C_{10}H_6$·SO_3H and its Me ester (total yield of sulphonation products 76%). CH_2Ph·OMe and aliphatic ethers such as di*iso*amyl ether are not sulphonated and undergo decomp. with formation of Me_2O and SO_2. G. A. R. K.

Phenol- and amino-plasties. I. Phenol-alcohols and their reaction with amines [and carbamide]. H. von Euler and H. Nyström (*J. pr. Chem.*, 1941, [ii], **159**, 121—129).—1 : 4 : 6 : 2-OH·$C_6H_2Me_2$·CH_2·OH (I) and $CO(NH_2)_2$ (II) in boiling aq. acid (p_H~2) afford 2-*hydroxy*-3 : 5-*dimethylbenzylcarbamide*, m.p. 192·5°. 1 : 4 : 2 : 6-OH·$C_6H_2Me(CH_2·OH)_2$ (III) and (II) yield 3 : 5-*di*(*carbamidomethyl*)-*p-cresol*, m.p. 210·5°, whilst 1 : 2 : 6 : 4-OH·$C_6H_2Me_2$·CH_2·OH and (II) afford s-*di*-(4-*hydroxy*-3 : 5-*dimethylbenzyl*)*carbamide*, m.p. 213°. (I) and NH_2·CO·NHMe afford N-2-*hydroxy*-3 : 5-*dimethylbenzyl*-N- (or N'-)*methylcarbamide*, m.p. 149·5°. (I) (2 mols.) with $(CH_2·NH_2)_2$ (IV) (1 mol.) in alkaline solution gives NN'-*di*-(2-*hydroxy*-3 : 5-*dimethylbenzyl*)*ethylenediamine*, m.p. 100°, but (III) and (IV) afford similarly 2 : 2'-*dihydroxy*-5 : 5'-*dimethyl*-3 : 3'-*di*(*hydroxymethyl*)*diphenylmethane*. (I) with boiling N_2H_4,H_2O (5 mols.) yields 2-hydroxy-3 : 5-dimethylbenzylhydrazine (an oil) (ON-*Ac*$_2$ derivative, m.p. 162°) and with NHPh·NH_2 yields α-*phenyl*-β-2-*hydroxy*-3 : 5-*dimethylbenzylhydrazine*, m.p. 104°. (I) and NH_2Ar,HCl give 2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2·NHAr [Ar = Ph, m.p. 85° (NO-derivative, m.p. 118·5°); Ar = *p*-C_6H_4Me, m.p. 99°]. Resins are formed from (I) or (III) and *p*-NH_2·C_6H_4·OH. C. S.

Hydrogenation of diaryl disulphides.—See B., 1942, II, 313.

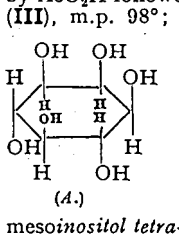
Catalytic hydrogenation of organic compounds. II. Benzaldehyde. III. Aromatic carbonyl compounds. K. Akashi (*Bull. Inst. Phys. Chem. Res. Japan*, 1941, **20**, 556—562, 563—568).—With Ni–Cu–Al_2O_3–kieselguhr catalysts supported on Cu wire, vapour-phase hydrogenation of PhCHO, *p*-C_6H_4Me·CHO, *o*-OMe·C_6H_4·CHO, piperonal, CHPh:CH·CHO, and COPhMe affords (mainly) the corresponding alcohol; $COPh_2$ yields CH_2Ph_2. F. O. H.

Reactions of propargyl derivatives. K. Zeile and H. Meyer (*Ber.*, 1942, **75**, [*B*], 356—362).—CH:C·CH_2Br, Zn, and *cyclo*hexanone (I) give γ-1-*hydroxy*cyclo*hexyl*-Δ^{α}-*propinene*, b.p. 80—83°/10 mm., m.p. 56·5° [hydrogenated (Pd-black in EtOH) to 1-propyl*cyclo*hexanol], 2-*cyclo*hexylidene*cyclo*hexanone, b.p. 95—96°/0·17 mm. (semicarbazone, m.p. 192—194°), and αγ-*di*-1-*hydroxy*cyclo*hexyl*-Δ^{α}-*propinene*, m.p. 113° [*di*-3 : 5-*dinitrobenzoate*, m.p. 159·5°; *diacetate* (II), b.p. 155—157°/0·6 mm.], which is hydrogenated (Pd-black in EtOH) to αγ-*di*-1-*hydroxy*cyclo*hexylpropane*, m.p. 120°, and (Pd-black in AcOH) to α-*cyclo*hexyl-γ-1-hydroxy*cyclo*hexylpropane, an oil (3 : 5-*dinitrobenzoate*, m.p. 88°). Addition of 1 H_2 (Pd-black, MeOH) to (II) and treatment of the product with $(CH_2·CO)_2O$ gives an *adduct*, $C_{21}H_{28}O_5$, m.p. 141·5°. Successive addition of CH:C·CH_2·OH (III) and (I) in C_6H_6 to MgEtBr in Et_2O yields γ-1-*hydroxy*cyclo*hexyl*-Δ^{β}-*propinen*-α-ol, b.p. 130—134° 0·5 mm., m.p. 51° (*formate*, b.p. 149—150°/12 mm.; *monobenzoate*, b.p. 166—167°/4 mm., m.p. 47°; *diacetate*, b.p. 151—155°/11·5 mm.). (III) and $MeSO_2Cl$ in 30% NaOH give the *methanesulphonate*, b.p. 109—110°/13 mm.; *p*-$C_6H_4Me·SO_2Cl$ and well-cooled 20% NaOH afford the p-*toluenesulphonate*, b.p. 117—120°/0·3 mm. *CPh*$_3$ *propargyl ether*, m.p. 111°, is converted by MgEtBr into *CPh*$_3$ δδδ-*triphenyl*-Δ^{β}-*butinenyl ether*, m.p. 191°, hydrogenated (Pd-black in C_6H_6) to *CPh*$_3$ δδδ-*triphenyl*-n-*butyl ether*, m.p. 181—182°. H. W.

Preparation of quinitol semiesters and of 4-hydroxy*cyclo*hexanone. K. Dimroth, E. Schmeil, and W. Daake *Ber.*, 1942, **75** [*B*], 317—321).—The mixture of quinitol (I) with its mono- and di-acetate is treated with BzCl in C_5H_5N and the product is hydrolysed with H_2SO_4–EtOH, whereby only Ac is removed, leaving a residue containing (I), *cis*- (II) and *trans*- (III) -mono-, and the isomeric di- (IV) -benzoates. (IV) are mainly pptd. when the alcoholic solution of the mixture is cooled and (I) remains in the aq. liquors when the filtrates are diluted and extracted with Et_2O. The residue readily deposits (III), m.p. 86°, whereas (II) is isolated with greater difficulty. Oxidation (CrO_3 in AcOH) of (II) or (III) gives 4-*keto*cyclo*hexyl benzoate*, b.p. 142°/0·02 mm., m.p. 63—64° (2 : 4-*dinitrophenylhydrazone*, m.p. 161°). The prep. of 4-keto*cyclo*hexyl acetate by oxidising (I) in Ac_2O with CrO_3 (Sabetay *et al.*, A., 1930, 1179) is unsatisfactory. H. W.

Phenol–formaldehyde resins. III. Quinonemethides as intermediates in the hardening process. K. Hultzsch (*J. pr. Chem.*, 1941, [ii], **159**, 155—179).—Four phenol-alcohols have been found to behave like 2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2·OH (*o*-hydroxymesityl alcohol) on heating. *p*-Cresol, *cyclo*hexanol, and 72% H_2SO_4 at 60° afford 3-*cyclo*hexyl-*p*-cresol, b.p. 160—170°, converted into 2-*hydroxy*-3-cyclo*hexyl*-5-*methylbenzyl alcohol* (I), m.p. 66·5°. 2 : 5 : 3 : 1-OH·$C_6H_2MeBu^{\gamma}$·CH_2·OH (II), an oil, is also prepared. 2-Hydroxy-5-*cyclo*hexyl-3-methylbenzyl alcohol (III) at 175°/2 hr. yields *di*-(2-*hydroxy*-5-cyclo*hexyl*-3-*methylbenzyl*) *ether*, m.p. 145°, which at 190—200°/30 mm. gives trimeric 5-cyclo*hexyl*-3-*methyl*-o-*quinonemethide* (IV), amorphous, m.p. 140°. At 240°, (III) gives 2-hydroxy-5-*cyclo*hexyl-3-methylbenzaldehyde, b.p. 150—160°/1·5 mm. (*semicarbazone*, m.p. 196°), a *compound*, $C_{30}H_{10}O_2$, m.p. 157° (*diacetate*, m.p. 168°) [also obtained from CH_2O and 5-*cyclo*hexyl-*o*-cresol in EtOH–conc. HCl together with *di*-(2-*hydroxy*-5-cyclo*hexyl*-3-*methylphenyl*)*methane* (V), m.p. 106—108° (*diacetate*, m.p. 125°)], and a residue, m.p. ~114°. (V) is obtained from (III) and boiling dil. aq. NaOH. (III) with AcOH–HCl affords 2-hydroxy-5-*cyclo*hexyl-3-methylbenzyl chloride, which with aq. Na_2CO_3–Et_2O gives (IV) (m.p. 120—130°). 2 : 3 : 5 : 1-OH·$C_6H_2MeBu^{\gamma}$·CH_2·OH (VI) at 160° affords CH_2O and *di*-(2-*hydroxy*-3-*methyl*-5-tert.-*butylbenzyl*) *ether*, m.p. 131·5° (*diacetate*, m.p. 143°); the residue with NaOH yields dimeric 3-*methyl*-5-tert.-*butyl*-o-*quinonemethide* (VII), m.p. 50°. At 240°, (VI) gives 2 : 3 : 5 : 1-OH·$C_6H_2MeBu^{\gamma}$·CHO, b.p. 115°/2 mm. (*semicarbazone*, m.p. 168—181°), αβ-*di*-(2-*hydroxy*-3-*methyl*-5-tert.-*butylphenyl*)*ethane*, b.p. 225—230°/2 mm., m.p. 72° (*diacetate*, m.p. 113·5°), and a residue, m.p. ~100°. 2 : 4 : 1-$C_6H_3MeBu^{\gamma}$·OH and CH_2O afford *di*-(2-*hydroxy*-3-*methyl*-5-tert.-*butylphenyl*)*methane*, m.p. 140° (*diacetate*, m.p. 70—71°). (VI) and AcOH–HCl afford 2-*hydroxy*-3-*methyl*-5-tert.-*butylbenzyl chloride*, converted (Na_2CO_3–Et_2O) into (VII) (m.p. 57°). (I) at 200° yields *di*-(2-*hydroxy*-3-cyclo*hexyl*-5-*methylbenzyl*) *ether* (VIII), m.p. 172·5°, and polymeric 3-cyclo*hexyl*-5-*methyl*-o-*quinonemethide* (IX), m.p. 175°. At 240°, (I) gives 2-*hydroxy*-3-cyclo*hexyl*-5-*methylbenzaldehyde*, b.p. 160—170°/2 mm., m.p. 128·5°, a xanthen *derivative*, $C_{27}H_{34}O$, m.p. 215°, αβ-*di*-(2-*hydroxy*-3-cyclo*hexyl*-5-*methylphenyl*)*ethane*, m.p. 137° (*diacetate*, m.p. 137°), and a residue, m.p. ~120°. *Di*-(2-*hydroxy*-3-cyclo*hexyl*-5-*methylphenyl*)*methane* (*diacetate*, m.p. 158°) has m.p. 134°. (I) and AcOH–HCl give the *chloride*, b.p. 175°/1·5 mm., m.p. 55—56° [another experiment gave (VIII)], converted (Na_2CO_3–Et_2O) into (IX). At 155°, (II) affords *di*-(2-*hydroxy*-5-*methyl*-3-tert.-*butylbenzyl*) *ether*, m.p. 93°, and ? *di*-(2-*hydroxy*-5-*methyl*-3-tert.-*butylphenyl*)*methane* (X), m.p. 131° [alkali-insol.; also obtained from 4 : 2 : 1-$C_6H_3MeBu^{\gamma}$·OH (XI), m.p. 53·5° (lit. 44°), and CH_2O in EtOH–conc. HCl; *mono*- or *di*-*acetate*, m.p. 110—112°; *mono*- or *di*-*benzoate*, m.p. 148°]. At 235°, (II) gives (X), (XI), resinous material, and a residue, m.p. 100°. C. S.

Acetonisation and configuration of *meso*inositol. G. Dangschat (*Naturwiss.*, 1942, **30**, 146—147).—*meso*Inositol (I) with a large excess of $COMe_2$ containing 10% of $ZnCl_2$ and 10% of AcOH followed by acetylation with Ac_2O–C_5H_5N gives iso*propylidene*meso*inositol tetra-acetate*, m.p. 123—124°, hydrolysed by NH_3–MeOH to iso*propylidene*meso*inositol*, decomp. 182—183°, by dil. HCl to meso*inositol tetra-acetate* (II), m.p. 132—133°, and by successive hydrolyses with acid and alkali to (I). (II) is indifferent to HIO_4 in AcOH but is oxidised by $Pb(OAc)_4$ in warm C_6H_6 to a non-cryst. dialdehyde (*bisphenylhydrazone*, decomp. 154°; *bis*-p-*nitrophenylhydrazone*, decomp. 183°; *bisdinitrophenylhydrazone*, decomp. 232°), converted by Ac_2O followed by diazoethane into *Et*$_2$ r-*tetra-acetylidosaccharate* (III), m.p. 98°; r-*idosaccharic acid* (IV) (*diamide*, decomp. 185—186°, and its *tetra-acetate*, m.p. 199°; *bisphenylhydrazide*, decomp. 214°) is non-cryst. The K salt appears to be transformed by AcOH into the K salt of a lactonic acid. *l*- and *d*-Xylose are converted by addition of HCN and oxidation into the active idosaccharic acids which when acetylated, esterified (diazoethane), and mixed in equal proportions give (III), thus confirming the constitution of (IV). (I) is therefore (*A*). *Methylene*-meso*inositol tetra-acetate* has m.p. 112°. H. W.


(*A.*)

Separated auxo-enoid systems. XVI. Colour of β-2 : 4-dinitrophenylpropionates and *p*-nitrocinnamates of phenols containing an additional auxo-group, and conclusions from previous investigations.

V. A. Izmailski and A. V. Belotzvetov (*J. Gen. Chem. Russ.*, 1941, **11**, 691—706; cf. A., 1942, II, 258).—β-2 : 4-Dinitrophenylpropionates of phenols containing an additional auxo-group (OH, OMe, NHAc) in the *p*-position are colourless except that of the *p*-NMe_2·C_6H_4 ester (**I**), which is orange-yellow. The corresponding *p*-nitrocinnamates are much darker and approximate to the 3 : 5-dinitrobenzoates in depth of colour. The colour of (**I**) shows that the coloration of the *p*-nitrobenzoates and the corresponding arylamides cannot be attributed to mesomerism in the groups –CO·O– and –CO·NH–, but to (probably intermol.) complex formation between the auxonoid and the nitro-enoid systems. The order of intensity of colour is explained by the structural conditions affecting these systems. Acyl groups form the series β-*p*-nitrophenylpropionyl (and *p*-nitrophenylacetyl) < β-2 : 4-dinitrophenylpropionyl < *p*-NO_2·C_6H_4·CO < *p*-nitrocinnamoyl and 3 : 5-$(NO_2)_2C_6H_3$·CO in order of their chromophoric effect. Structural conditions are discussed in the light of mesomerism and the principle of counter-polarising effects. The weakening of the auxochromic power of N and O atoms on acylation is attributed to the scattering of the electromeric effect.

The following have been prepared: p-*nitrocinnamoyl chloride*, m.p. 150·5—152·5°; β-2 : 4-dinitrophenylpropionyl chloride, m.p. 127—128·5°; *p*-nitrocinnamates: Ph, m.p. 152·2—152·7°, p-*anisyl*, m.p. 157·1—157·5°, p-*dimethylaminophenyl*, m.p. 198·8—199·5°, p-*acetamidophenyl*, m.p. 235—235·5° (also a colourless form converted into the yellow at ~100°), *quinol mono-*, m.p. 217—218·2°, and *di-*, m.p. 322—323°; β-2 : 4-*dinitrophenylpropionates*: *Ph*, m.p. 84—84·4°, p-*anisyl*, m.p. 105·3—105·8°, p-*dimethylaminophenyl*, m.p. 120·3—120·7°, *quinol mono-*, m.p. 142·7—144°, and *di-*, m.p. 179—181°. G. A. R. K.

Iodinated organic compounds as contrast media for radiographic diagnoses. I. Iodinated aracyl esters. W. H. Strain, J. T. Plati, and S. L. Warren (*J. Amer. Chem. Soc.*, 1942, **64**, 1436—1440).—RCO_2Na and CH_2Cl·CO_2R' at 160—170° give *Et* o-*iodobenzoyloxy*- (63%), b.p. 169°/0·02 mm., β-p-*iodophenylpropionoxy*- (51%), m.p. 41—42°, and *undecenoyloxy*- (61%), b.p. 145°/0·2 mm., and *ethylene glycol di*-o-*iodobenzoyloxy*- (69%), m.p. 80—81°, -*acetate* but κ-I·$C_{10}H_{20}$·CO_2Na gives tars. $(CH_2Cl·CO_2·CH_2)_2$ is obtained (35%) from $(CH_2·OH)_2$, $CH_2Cl·CO_2H$, and $ZnCl_2$ at 100°. *p*-$C_6H_4I·CH_2Br$, $CH_2(CO_2Et)_2$, and NaOEt–EtOH give *Et* p-*iodobenzylmalonate* (54%), b.p. 180—183°/3 mm., and thence (alkali; 80% EtOH) the derived acid, m.p. 164—165° (decomp.), and (at 160—170°) *p*-$C_6H_4I·[CH_2]_2·CO_2H$. *o*-$C_6H_4I·OH$ (**I**) and $Br·[CH_2]_3$·Br in boiling aq. NaOH give *o*-$C_6H_4I·O·[CH_2]_3$·Br (58%), b.p. 154—156°/0·2 mm., and thence (NaCN) the nitrile (55%), b.p. 160°/0·2 mm., and (H_2SO_4–EtOH) *Et* γ-*o-iodophenoxy*-n-*butyrate* (~100%), b.p. 158°/0·1—0·2 mm. $(CH_2Br)_2$ (2 mols.) and (**I**) (1 mol.) with NaOEt (1 mol.) in boiling EtOH give β-*o-iodophenoxyethyl bromide* (34%), m.p. 50—51°, and αβ-*di*-o-*iodophenoxyethane* (10%), m.p. 120—121°. κ-Br·$C_{10}H_{20}$·CO_2Et and *o*-$C_6H_4I·ONa$ at ~110° give *Et* κ-*o-iodophenoxyundecoate* (48%), b.p. 235—240°/2 mm., and thence the *acid*, m.p. 49—50·5°. $C_{10}H_{19}$·CO_2Et, PhI, and $AlCl_3$ at 0—8° give mixed *Et iodophenylundecoates* (**II**) (40%), b.p. 205—213°/1·5 mm. (and di-condensation products), giving by hydrolysis and subsequent oxidation 12% of *p*-$C_6H_4I·CO_2H$; PhBr gives similarly mixed *Et bromophenylundecoates* (45%), b.p. 186—189°/1·5 mm. PhI, Et oleate, and $AlCl_3$ give *Et iodophenylstearate* (22%; ? pure), b.p. 242—258°/2 mm. $(CH_2·CO)_2O$, PhI, and $AlCl_3$ give exothermally a mixture including γ-*keto*-γ-p-*iodophenyl*-n-*butyric acid* (13%), m.p. 177—178° [*Et* (**III**), m.p. 64—65°, and *Me* ester, m.p. 67·5—68·5°], *p*- and *o*-$C_6H_4I_2$. Clemmensen reduction of (**III**) gives a poor yield of γ-p-*iodophenyl*-n-*butyric acid*, m.p. 89—89·5° [*Et* ester, b.p. 183°/10 mm.; oxidised to *p*-$C_6H_4I·CO_2H$ (63%)]. $CO_2Et·[CH_2]_4·COCl$, PhI, and $AlCl_3$ give similarly ε-*keto*-ε-p-*iodophenyl*-, m.p. 154—156° (*Et* ester, m.p. 66—67°), and ε-p-*iodophenyl*-n-*hexoic acid*, m.p. 66—67° (*Et* ester, b.p. 205—210°/10 mm.). Of the products, (**II**) is the best liquid contrast medium for radiographic purposes. R. S. C.

Stability of di-iodotyrosine solutions. K. Kraft and F. Dengel (*Z. physiol. Chem.*, 1942, **272**, 147—151).—Concns. of di-iodotyrosine >0·5% cannot be obtained by dissolution in org. and inorg. acids. Decomp. and conversion into thyroxine by alkali is almost entirely prevented by employing <2·1N. aq. NaOH. W. McC.

Reaction of the Grignard reagent with esters of highly hindered acids. R. C. Fuson, E. M. Bottorff, and S. B. Speck (*J. Amer. Chem. Soc.*, 1942, **64**, 1450—1453).—Alkyl (Me, CH_2Ph) mesitoates with MgRHal (R = $Bu^α$ or Ph) in Bu_2O give mesitoic acid (**I**) (25—65%) and alkyl halide (20—70%); with MgI 80—97% of (**I**) results. p-*Tolyl mesitoate* (**II**), m.p. 73°, with MgMeI or MeEtBr gives *p*-cresol (**III**) (76, 54%) and acetyl- (45%) or propionyl-mesitylene (61%), respectively. p-*Tolyl* 2 : 4 : 6-*triisopropylbenzoate*, m.p. 66—68°, b.p. 181—184°/3 mm., behaves similarly with MgMeI and MgEtBr, yielding (**III**) (78%) and 2 : 4 : 6-*triisopropyl-aceto*- (46%), m.p. 87·5—88°, and -*propio-phenone* (43%), m.p. 81—83°, b.p. 123—126°/3 mm., respectively; both ketones are also prepared by Friedel–Crafts reaction in CS_2 at 10°. Aryl mesitoates and MgArHal in Bu_2O give similarly first the phenol (40—95%) and ketone, but *o*-arylation of the ketone then occurs. Thus (**II**) with MgArBr gives 2-*mesitoyl*-5 : 4′-*dimethyldiphenyl* (13%), m.p. 101°, and *mesityl* 2-1′-*naphthyl*-1-*naphthyl* (a trace), m.p. 180°, 2′-*methoxy*-2-*diphenylyl* (13%), m.p. 94°, and 3′-*methoxy*-(? 5 : 3′-*dimethoxy*-)2-*diphenylyl* (6%), m.p. 144°, *ketone*. With 2 : 4 : 6 : 1-$C_6H_2Me_3$·MgBr, (**II**) gives (**III**) (85%), dimesityl ketone (3%) and diketone (**IV**) (a trace). With CH_2Ph·MgCl, (**II**) gives (**III**) (55%) and a small amount of (**IV**). Bu, b.p. 119—121°/3 mm., and *CH_2Ph mesitoate*, m.p. 38—39°, b.p. 164—169°/2·5 mm., are described. M.p. are corr. R. S. C.

Inter-relation of first- and second-order asymmetric transformations. (Miss) M. M. Jamison and E. E. Turner (*J.C.S.*, 1942, 437—440; cf. A., 1940, II, 173).—Corbellini and Angeletti's work (A., 1933, 64) has been repeated on 2′-(α-hydroxy*iso*propyl)diphenyl-2-carboxylic acid (**I**) (improved prep.). Discrepancies in the mutarotation results for the brucine *l*-acid salt (**II**) in $CHCl_3$ are attributed to the formation of the optically inactive lactone, m.p. 124—125°, of (**I**). The brucine salt of (**I**) undergoes first-order asymmetric transformation in $CHCl_3$ [brucine *d*-acid salt optically more stable; hence (**II**) separates first]; the experiments recorded constitute the first example of the application of the van't Hoff–Dimroth rule to asymmetric transformation in which both first- and second-order changes can be realised. Mutarotation is also observed in dextro-direction with quinidine and *dl*-(**I**) in mol. proportions in $CHCl_3$, and lævo- with quinine or cinchonidine. C. S.

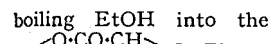
Conjugated diolefines.—See A., 1942, II, 293.

Isomerism of disalicylides. II. Re-examination of the data concerning the composition and mol. wt. of β-disalicylide. L. Anschütz and A. Mayer (*J. pr. Chem.*, 1942, [ii], **159**, 343—344).—Elementary analyses and determinations of the mol. wt. of β-disalicylide in camphor, dioxan, PhOH, and $CHCl_3$ confirm the formula, $C_{14}H_8O_4$. The two disalicylides are therefore isomerides. H. W.

Preparation of acetylsalicylyl and salicylyl disulphides. B. Riegel and H. Wittcoff (*J. Amer. Chem. Soc.*, 1942, **64**, 1486—1487).—*o*-OAc·C_6H_4·COCl (prep. by $SOCl_2$–C_5H_5N), b.p. 115°/5 mm., m.p. 52° (turbid), 60° (clear), with anhyd. NaSH–EtOH (prep. described) and then I–EtOH gives *disalicylyl disulphide* (**I**), m.p. 142° (Pyrex), which with Ac_2O and a little H_2SO_4 at room temp. gives the *diacetate* (**II**), m.p. 101·2°. M.p. are corr. (**I**) and (**II**) are non-toxic but do not appear to have much antipruritic activity. R. S. C.

Naphtol AS series. V. Synthetic experiments. II. R. V. Bhat and K. Venkataraman (*J. Soc. Dyers and Col.*, 1942, **58**, 155—161; cf. B., 1940, 428).—2 : 3-OH·$C_{10}H_6$·COCl (**I**) and *p*-$C_6H_4Me·SO_2·NMe·C_6H_4·NH_2$-*m* or -*p* in solvent naphtha or $C_2H_2Cl_4$ respectively, at 150—160°, afford *toluene*-p-*sulphon*-N-*methyl*-m′-, m.p. 212—213°, or -p′-2″-*hydroxy*-3″-*naphthoylaminoanilide*, m.p. 230°, respectively. Similarly prepared from (**I**) and the appropriate base are: *toluene*-p-*sulphon*-p′-2″-*hydroxy*-3″-*naphthoylaminoanilide*, m.p. 261—262°; 2-2′-*hydroxy*-3′-*naphthoylaminothiazole*, m.p. 299—300° (decomp.); 1 : 2-*di*-2′-*hydroxy*-3′-*naphthoylaminonaphthalene*, m.p. 296—297°; 8-(2′-*hydroxy*-3′-*naphthoylamino*)-1-*naphthylamine*, m.p. 264—265°; m-, m.p. 273—274°, and p-2′-*hydroxy*-3′-*naphthoylaminobenzanilide*, m.p. 290—291° (also obtained from p-2′-*hydroxy*-3′-*naphthoylaminobenzoic acid*, m.p. 315—316°, and NH_2Ph–C_5H_5N–PCl_3); 4-2′-*hydroxy*-3′-*naphthoylamino*-*acetophenone*, m.p. 263—264°, or -*benzophenone*, m.p. 255°. *Mono*-2-*hydroxy*-3-*naphthoyl*-m-*phenylenediamine*, m.p. 198—199°, and BzCl–dioxan give N′-*benzoyl*-N-2-*hydroxy*-3-*naphthoyl*-m-*phenylenediamine*, m.p. 281—282°, also prepared from (**I**) and *m*-$NH_2·C_6H_4·NHBz$. Substantivity and fastness tests are carried out on the compounds. A. T. P.

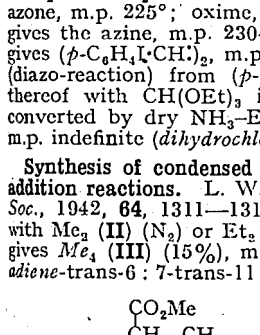
Molecular rearrangements involving optically active radicals. XI. Rearrangements in the truxillic acids and their bearing on theories of molecular rearrangements and optical rotatory power. H. I. Bernstein and E. S. Wallis (*J. Org. Chem.*, 1942, **7**, 261—273).—(+)-γ-Truxillamidic acid is converted by NaOCl at 38—40° followed by CO_2 into (−)-γ-truxillamic acid (**I**), m.p. 211—214° (decomp.) in bath at 200° {*hydrochloride*, m.p. 268° (decomp.); $[\alpha]^{20}_{6563}$ −16·6°, $[\alpha]^{20}_{5893}$ −22·7°, $[\alpha]^{20}_{5463}$ −28·8° in MeOH; *Me* ester *hydrochloride*, m.p. 269° (decomp.) in bath at 250°, $[\alpha]^{20}_{6563}$ −24·7°, $[\alpha]^{20}_{5893}$ −29·6°, $[\alpha]^{20}_{5463}$ −36·8° in MeOH}. (**I**) and NOBr in Et_2O at <−5° give the (+)-lactone, m.p. 138°, $[\alpha]^{20}_{6563}$ +11·2°, $[\alpha]^{20}_{5893}$ +15·5°, $[\alpha]^{20}_{5463}$ +19·6° in MeOH, whilst the (+)-acid yields the (−)-*lactone* (**II**), m.p. 139°, $[\alpha]^{20}_{6563}$ −10·2°, $[\alpha]^{20}_{5893}$ −14·4°, $[\alpha]^{20}_{5463}$ −19·5° in MeOH, $[\alpha]^{20}_{6563}$ +30·6°, $[\alpha]^{20}_{5893}$ +35·2°, $[\alpha]^{20}_{5463}$ +41·8° in C_6H_6. (**II**) and KOH–EtOH afford (−)-3^c-*phenyl*-2^c-α-*hydroxybenzylcyclopropane*-1^c-*carboxylic acid* (**III**), m.p. 150° (decomp.) if placed in bath at 141°, $[\alpha]^{20}_{6563}$ −78·4°, $[\alpha]^{20}_{5893}$ −101·4°, $[\alpha]^{20}_{5463}$ −121·4° in MeOH, whilst the (+)-OH-acid (**IV**) has m.p. 146°, $[\alpha]^{20}_{6563}$ +75·4°, $[\alpha]^{20}_{5893}$ +96·6°, $[\alpha]^{20}_{5463}$ +116·6° in MeOH. (**III**) and CH_2N_2 give (**II**) or, under somewhat different conditions, the *Me* ester of (**III**), m.p. 145° (decomp.), $[\alpha]^{20}_{6563}$ −89·4°, $[\alpha]^{20}_{5893}$ −118·5°, $[\alpha]^{20}_{5463}$ −141·7° in MeOH. (**IV**) yields the corresponding *Me* ester, m.p. 146°, $[\alpha]^{20}_{6563}$ +95°, $[\alpha]^{20}_{5893}$ +127°, $[\alpha]^{20}_{5463}$ +140° in MeOH, and an equimol. mixture of ester and lactone. Oxidation (CrO_3 in AcOH) of the (−)-Me ester gives *Me* (+)-2^c-*benzoyl*-3^c-*phenylcyclopropane*-1^c-*carboxylate*, m.p. 109°, $[\alpha]^{20}_{6563}$ +5·4°, $[\alpha]^{20}_{5893}$ +6·0°, $[\alpha]^{20}_{5463}$ +7·21° in MeOH, transformed by NH_2OH,HCl in

boiling EtOH into the corresponding (+)-*dihydro-orthoxazine*,  CHPh, m.p. 180°, $[\alpha]^{20}_{5563}$ +177°, $[\alpha]^{20}_{5893}$ +226°, $[\alpha]^{20}_{5463}$ +271° in MeOH. (**II**) and boiling 50% KOH–EtOH afford (+)-3^c-*phenyl*-2^c-*α-hydroxybenzyl*cyclo*propane*-1^1-*carboxylic acid*, m.p. 160° (decomp.), $[\alpha]^{20}_{5563}$ +43·2°, $[\alpha]^{20}_{5893}$ +56·4°, $[\alpha]^{20}_{5463}$ +68·3° in MeOH (Me ester, $[\alpha]^{20}_{5563}$ +47·3°, $[\alpha]^{20}_{5893}$ +60·6°, $[\alpha]^{20}_{5463}$ +73·2° in MeOH); the (−)-acid has m.p. 161—162° (decomp.), $[\alpha]^{20}_{5563}$ −43·3°, $[\alpha]^{20}_{5893}$ −56·0°, $[\alpha]^{20}_{5463}$ −67·8° in MeOH {Me ester (**V**), $[\alpha]^{20}_{5563}$ −47·4°, $[\alpha]^{20}_{5893}$ −61·4°, $[\alpha]^{20}_{5463}$ −74·9° in MeOH}. *Me* 2-*benzoyl*-3-*phenyl*cyclo*propane*-1-*carboxylate*, m.p. 85°, $[\alpha]^{20}_{5563}$ −121·2°, $[\alpha]^{20}_{5893}$ −158·6°, $[\alpha]^{20}_{5463}$ −192·5° in MeOH, is prepared from (**V**). The instances of Walden inversion recorded above are considered in terms of the electronic theory of mol. rearrangement. The direction of the shift in optical rotatory power in the formation of dicyclic lactones, imides, and lactams from the corresponding monocyclic acids is shown to be random; this behaviour is discussed in the light of newer theories of optical rotatory power. H. W.

Synthesis of 4 : 4′-dicyanostilbene. S. C. Fu and P. P. T. Sah (*J. Amer. Chem. Soc.*, 1942, **64**, 1482).—Pyrolysis of 4 : 4′-*dicyanobenzaldazine* (prep. from *p*-CN·C$_6$H$_4$·CHO by N_2H_4,H$_2$O in boiling abs. EtOH), m.p. 118—120°, gives 25% of (*p*-CN·C$_6$H$_4$·CH:)$_2$. R. S. C.

Synthesis of 4 : 4′-diamidinostilbene hydrochloride. P. P. T. Sah (*J. Amer. Chem. Soc.*, 1942, **64**, 1487—1488).—*p*-C$_6$H$_4$I·CHO (prep. by $SnCl_2$–HCl–Et_2O etc. from *p*-C$_6$H$_4$I·CN), m.p. 77—78° (semicarbazone, m.p. 225°; oxime, m.p. 111—112°) (cf. lit.), with N_2H_4,H$_2$O gives the azine, m.p. 230—232° (decomp.), which, when sublimed, gives (*p*-C$_6$H$_4$I·CH:)$_2$, m.p. 259—260° (lit. 257—259°), also obtained (diazo-reaction) from (*p*-NH$_2$·C$_6$H$_4$·CH:)$_2$. The Grignard reagent thereof with CH(OEt)$_3$ in Et$_2$O gives an impure, syrupy *ester*, converted by dry NH$_3$–EtOH at 30° into 4 : 4′-diamidinostilbene, m.p. indefinite (*dihydrochloride*, m.p. >300°). R. S. C.

Synthesis of condensed ring compounds. VIII. Di-inene double addition reactions. L. W. Butz and L. M. Joshel (*J. Amer. Chem. Soc.*, 1942, **64**, 1311—1313).—Di*cyclo*hexenylacetylene (**I**) (1 mol.) with Me$_2$ (**II**) (N$_2$) or Et$_2$ fumarate (CO$_2$) (>2 mols.) at, best, 175° gives *Me*$_4$ (**III**) (15%), m.p. 111·6—112·6°, and *Et*$_4$ $\Delta^{8(14):9}$-*chrysitadiene*-trans-6 : 7-trans-11 : 12-*tetracarboxylate* (7%), m.p. 90—91°.


(III.)

The adduct (A., 1942, II, 142) from (**I**) and (CH·CO)$_2$O is converted by N-KOH into $\Delta^{8(14):9}$-*chrysitadiene*-cis-6 : 7-cis-11 : 12-*tetracarboxylic acid* (97%), m.p. 256·5—258° (decomp.), which with CH_2N_2 gives the *Me*$_4$ ester [cf. (**III**)], m.p. 121—122·5°, hydrogenated (PtO_2, AcOH) to *Me*$_4$ Δ^8-*chrysitene*-cis-6 : 7-cis-11 : 12-*tetracarboxylate* (85%), m.p. 158—159°. (**III**) resists hydrogenation. *cyclo*Pentenyl-4-methoxy*cyclo*hexenylacetylene and (**II**) at 175° (N$_2$) give *Me*$_4$ 3-*methoxy*-$\Delta^{8(14):9}$-*steradiene*-trans-6 : 7-trans-11 : 12-*tetracarboxylate* (45%), b.p. ~150° (bath)/0·001 mm. M.p. are corr. R. S. C.

Condensation of aldehydes with amides. X. Condensation of *m*- and *p*-nitrobenzaldehyde and 2 : 4-dinitrobenzaldehyde. P. I. Ittyerah and K. C. Pandya (*Proc. Indian Acad. Sci.*, 1942, **15, A**, 258—263).—The aldehydes and amides (1 : 2) are heated at 130—140°, rapidity of reaction and yield diminishing in the sequence, $p > m > o$. 2 : 4 : 1-(NO$_2$)$_2$C$_6$H$_3$·CHO could not be condensed with NH$_2$Ac or NH$_2$Bz. The products do not give a colour with cold conc. H_2SO_4 and are hydrolysed by the hot, dil. acid. Attempted nitration causes decomp. The following are described: m-*nitrobenzylidenediformamide*, m.p. 168°, -diacetamide, m.p. 255—256° (lit. 236—237°), -*dipropionamide*, m.p. 220—221°, -*di*-n-*butyramide*, m.p. 194°, -*di*-n-*heptoamide*, m.p. 149°, -dibenzamide, m.p. 228—230° (lit. 224°), and -*bisphenylacetamide*, m.p. 214—216°; p-*nitrobenzylidene-diformamide*, m.p. 194° or (apparently polymerised) m.p. 210—220°, -*diacetamide*, m.p. 272°, -*dipropionamide*, m.p. 252°, -*di*-n-*butyramide*, m.p. 224°, -*di*-n-*heptoamide*, m.p. 170°, -*dibenzamide*, m.p. 258—259°, and -*bisphenylacetamide*, m.p. 248°. H. W.

Internally complex salts of α-amino-acid esters. P. Pfeiffer, W. Offermann, and H. Werner (*J. pr. Chem.*, 1942, [ii], **159**, 313—333).—The Cu derivative (**I**) of *o*-OH·C$_6$H$_4$·CHO with NH$_2$·CH$_2$·CO$_2$Et,HCl and anhyd. NaOAc in boiling EtOH affords *Cu Et salicylideneaminoacetate* (**II**), m.p. 200° (decomp.). *l*-Menthol and CH$_2$Cl·COCl in CHCl$_3$ afford *l-menthyl chloroacetate*, m.p. 38°, transformed by NH$_3$ in dioxan into *l-menthyl aminoacetate hydrochloride*, m.p. ~175°, which has normal rotation dispersion in H$_2$O; with (**I**) it gives a *Cu* complex, $C_{36}H_{52}O_6N_2Cu$, which shows a marked Cotton effect. Similarly the Ni complex (**III**) of *o*-OH·C$_6$H$_4$·CHO and NH$_2$·CH$_2$·CO$_2$Et affords the *complex*, $C_{22}H_{24}O_6N_2Ni$, m.p. 230° (decomp.), and the *l-menthyl* complex, $C_{36}H_{52}O_6N_2Ni$. Alanine and *l*-phenylalanine Et esters yield the analogous *complexes*, $C_{21}H_{26}O_6N_2Cu$ and optically inactive $C_{36}H_{38}O_6N_2Cu$. *o*-OH·C$_6$H$_4$·CHO, Cu(OAc)$_2$, NaOAc, and *l*-ornithine dihydrochloride in EtOH give the *compound*, $C_{28}H_{34}O_8N_4Cu_3$ (also +3C$_5$H$_5$N). Similarly *l*-lysine dihydrochloride gives the *complex*, $C_{20}H_{20}O_4N_2Cu$ (+1 or 2C$_5$H$_5$N), and its Et ester affords the *salt*, $C_{22}H_{24}O_4N_4Cu$. (**I**) and (**III**) with *l*-leucine Et ester in presence of air give the salicylaldehydeimine *compounds*, $C_{14}H_{12}O_2N_2Cu$ and $C_{14}H_{12}O_2N_2Ni$ (**IV**). Attempts to isolate a normal condensation product from (**III**) and *l*-phenylalanine ester were unsuccessful; (**IV**) is isolable. The Cu compound of 2 : 1-OH·C$_{10}$H$_6$·CHO with NH$_2$·CH$_2$·CO$_2$Et,HCl and anhyd. NaOAc in boiling EtOH give the *complex*, $C_{30}H_{28}O_6N_2Cu$ (**V**), decomp., ~186°. (**II**) and the corresponding Ni compound readily undergo ester-interchange. Thus in boiling MeOH they give the *Me* esters, $C_{20}H_{20}O_6N_2Cu$, m.p. 213° (decomp.), and $C_{20}H_{20}O_6N_2Ni$, m.p. 236° (decomp.). The reaction is reversible. The *Pr*^{a} esters, m.p. 182° (decomp.) and 208° (decomp.), respectively are obtained from the Et esters but the reverse change does not appear to take place. The *Bu*^{a} esters, m.p. 166° (decomp.) and 203° (decomp.), respectively, are obtained from the Et esters and also directly from NH$_2$·CH$_2$·CO$_2$Bu,HCl. The iso*amyl* ester, $C_{28}H_{36}O_6N_2Ni$, has m.p. 194—195° (decomp.). Re-esterification with CH$_2$Ph·OH appears more difficult. (**V**) gives the *Bu* ester, $C_{34}H_{36}O_6N_2Cu$, softens ~177°. H. W.

Vanillin from lignin materials. [Its determination.] I. A. Pearl (*J. Amer. Chem. Soc.*, 1942, **64**, 1429—1431).—The solids from sulphite waste liquor or BuOH-lignin with aq. CuSO$_4$–NaOH or –CaO at 160° or, less well, the b.p. give 9·7—21·9% of vanillin (**I**). "Meadol" gives also syringaldehyde [~3 parts for each part of (**I**)]. (**I**) is best determined as 2 : 4-dinitrophenylhydrazone, the acidity not being crit. R. S. C.

Phenol–formaldehyde resins. IX. Formation of aldehyde groups during the hardening of phenoldialcohols. K. Hultzsch and G. Schiemann (*Ber.*, 1942, **75**, [*B*], 363—368).—1 : 4 : 2 : 6-OH·C$_6$H$_2$Bu$^\gamma$(CH$_2$·OH)$_2$ when heated in CO$_2$ at 230° evolves CH$_2$O and H$_2$O giving a residue which at 120—160°/2 mm. gives a distillate containing 2-*hydroxy*-5-tert.-*butylisophthalaldehyde*, m.p. 105·5° (*dioxime*, m.p. 184—185·5°), 2-*hydroxy*-3-*methyl*-5-tert.-*butylbenzaldehyde* (**I**), m.p. 44—45°, and 2 : 6 : 4 : 1-C$_6$H$_2$Me$_2$Bu$^\gamma$·OH, m.p. 80°. The residue from the distillation contains ·CHO. Similarly 2 : 6-di(hydroxymethyl)-4-*aaγγ*-tetramethyl-*n*-butylphenol at 230° yields H$_2$O and CH$_2$O and the residue on distillation affords 2-hydroxy-5-*aaγγ*-tetramethyl-*n*-butyl*iso*phthalaldehyde (*dioxime*, m.p. 168°), and 2-hydroxy-3-methyl-5-*aaγγ*-tetramethyl-*n*-butylbenzaldehyde (*oxime*, m.p. 123—126°); the non-volatile residue contains ·CHO. (**I**) is obtained from 2 : 3 : 5 : 1-OH·C$_6$H$_2$MeBu$^\gamma$·CH$_2$·OH and *m*-NO$_2$·C$_6$H$_4$·SO$_3$Na in boiling 10% NaOH. ·CHO is not present in the resin from *o*-hydroxymesityl alcohol but is abundantly formed when 1 : 4 : 2 : 6-OH·C$_6$H$_2$Me(CH$_2$·OH)$_2$ is hardened between 155° and 230°. H. W.

Phenoxyacetones. D. S. Tarbell (*J. Org. Chem.*, 1942, **7**, 251—260).—*p*-C$_6$H$_4$Me·O·CH$_2$·COMe (**I**), b.p. 107—109°/5 mm. (*semicarbazone*, m.p. 179—180°), prepared from *p*-C$_6$H$_4$Me·ONa and CH$_2$Br·COMe in C$_6$H$_6$ or by ozonisation of *p*-C$_6$H$_4$Me·O·CH$_2$·CMe:CH$_2$, is largely unchanged at 250—260° if pure, yielding only a small proportion of *p*-cresol. 2 : 4 : 1-CH$_2$:CMe·CH$_2$·C$_6$H$_3$Me·OH is ozonised to 2 : 4 : 1-COMe·CH$_2$·C$_6$H$_3$Me·OH [*semicarbazone*, m.p. 187—188° (decomp.)]. 2 : 6-Dimethylphenoxyacetone (**II**), b.p. 110—113°/4 mm. (*semicarbazone*, m.p. 163—165°), gives *m*-2-xylenol when kept and is partly decomposed when heated at 200—205° for 1 hr. 2 : 4-Dimethyl- (**III**), b.p. 120°/6 mm. (*semicarbazone*, m.p. 143—144·5°), p-*bromo*- (**IV**), m.p. 42·5—44° (*semicarbazone*, m.p. 196—205° depending on the rate of heating), *o*-nitro- (**V**), *m*-nitro- (**VI**), m.p. 79—81° (lit. 83—84°), *p*-nitro- (**VII**), 6-*nitro*-2 : 4-*dimethyl*- (**VIII**), m.p. 68—69°, and 4-*nitro*-2 : 6-*dimethyl*- (**IX**), m.p. 111·5—113° [semicarbazone, m.p. 197—199° (decomp.)], -*phenoxyacetone* are described. (**I**) and (**II**) do not rearrange when heated. The phenoxyacetones can be partly extracted from C$_6$H$_6$ or light petroleum by Claisen's alkali; (**VII**) and (**IX**) are thus cleaved, giving the corresponding nitrophenols, whereas (**V**) and (**VIII**) undergo complete decomp. (**VI**) is extracted from C$_6$H$_6$ without cleavage and its acidity is attributed to the increase of the electron-attracting effect of the OPh group by NO$_2$ making H attached to C next to the ether O more acidic. (**VII**) and (**IX**) are cleaved by NaOMe in MeOH at room temp. at about the same rate whilst (**V**) is decomposed very much more rapidly and (**IV**) is scarcely affected. M.p. are corr. H. W.

Mechanism of the haloform reaction. Preparation of mixed haloforms. J. G. Aston, J. D. Newkirk, J. Dorsky, and D. M. Jenkins (*J. Amer. Chem. Soc.*, 1942, **64**, 1413—1416).—Prep. of COPh·CCl$_3$ (**I**) from COPh·CHCl$_2$ by Cl$_2$–AcOH and of *aaa-tribromoacetophenone* (**II**), m.p. 65—66°, from COPhMe by Br–AcOH requires addition of NaOAc. In 5N-NaOH at 0°, (**II**) is stable and (**I**) is only slowly decomposed; decomp. of (**II**) in N-NaOH at 80° is slow; however, decomp. of (**II**) by NaOH (1 mol.) in 1 : 2 H$_2$O–dioxan is rapid. Differences are due to relative solubilities. Similarly, some (**I**) is obtained when COPh·CHCl$_2$ is treated with NaOCl–NaOH, particularly if little NaOH is used, and (**I**) is the sole product at 0°. COPh·CH$_2$Cl and Br–AcOH–NaOAc give COPh·CCl$_2$Br (30%) and (**II**) (formed by interaction with NaBr), the amounts formed being determined by cleavage by NaOAc–MeOH to CHCl$_2$Br and CHBr$_3$. COPh·CHCl$_2$ and NaBr in AcOH give COPh·CHClBr. R. S.

p-Dimethylaminobenzylidene derivatives of 3 : 5-dinitro-2 : 6-dimethyl-4-*tert.*-butylacetophenone (musk ketone) and 2 : 6-dimethyl-4-*tert.*-butylacetophenone. A. Müller (*J. pr. Chem.*, 1941, [ii], **159**, 139—145).—3 : 5 : 2 : 6 : 4 : 1-$(NO_2)_2C_6Me_2Bu^{\gamma}$·COMe (I) and *p*-$NMe_2$·$C_6H_4$·CHO (II) in 4% EtOH–NaOEt afford 3 : 5-*dinitro*-2 : 6-*dimethyl*-4-tert.-*butylphenyl* p-*dimethylaminostyryl ketone* (III), reddish-yellow, m.p. 204·5—205·5° (corr.); 1 mg. of (I) is detectable. (III) (solid; in EtOH or AcOH) shows green fluorescence in filtered ultra-violet light. 2 : 6 : 4 : 1-$C_6H_2Me_2Bu^{\gamma}$·COMe and (II) similarly give 2 : 6-*dimethyl*-4-tert.-*butylphenyl* p-*dimethylaminostyryl ketone* (IV), yellow-green, m.p. 126·5° (corr.) (red-orange salts), which (as above) shows yellow-green fluorescence. (I) does not react with the *EM* reagent (cf. A., 1939, II, 329) in acid solution. Colourless salts of (III) are due to the addition of a proton to N and not CO. Coloured salts of (IV) result from a mesomeric system.
$CO(C_6H_4$·NMe_2-*p*$)_2$ and *p*-NO·C_6H_4·NMe_2 do not condense with β-ionone or (I) and are unsuitable as substitutes for (II) in the *EM* reagent. C. S.

1-Methylphenanthrene series. III. Synthesis of 3-acetyl-1-methylphenanthrene. T. Hasselstrom and D. Todd (*J. Amer. Chem. Soc.*, 1942, **64**, 1225—1226; cf. A., 1942, II, 9).—Addition of $AlCl_3$ to 1-methylphenanthrene and AcCl in $PhNO_2$ at 0° gives 3-*acetyl*-1-*methylphenanthrene*, m.p. 111·5—112·5° [*picrate*, m.p. 137—137·5°; structure proved by oxidation by HNO_3–H_2O at 190° to 1 : 2 : 3 : 5-$C_6H_2(CO_2H)_4$], the *oxime* (I), m.p. 180·5—181°, of which with PCl_5–Et_2O at 15—20° gives 3-*acetamido*-1-*methylphenanthrene*, m.p. 188·5—189·5° (with boiling Ac_2O–NaOAc yields the Ac_2 compound, m.p. 162—162·5°). With dry HCl–AcOH–Ac_2O and then HCl–AcOH–H_2O, (I) gives 3-*amino*-1-*methylphenanthrene*, m.p. 126—127° (uncorr.), and thence 1-*methyl*-3-*phenanthrol*, m.p. 160—161°. M.p. are corr. R. S. C.

Oxidation of benzophenoxime. W. M. Lauer and W. S. Dyer (*J. Amer. Chem. Soc.*, 1942, **64**, 1453—1456).—CPh_2:N·OH and $K_3Fe(CN)_6$ in KOH–EtOH–H_2O at 35° give $COPh_2$, diphenylketazine oxide, CPh_2:N·N(→O):CPh_2 (I), m.p. 156—159°, yellow, and (?) the *benzophenoxime* ester of *aci*-nitrodiphenylmethane, CPh_2:N·O·N(→O):CPh_2 (II), m.p. 193° (decomp.) (cf. Hunter *et al.*, A., 1934, 191; von Auwers *et al.*, A., 1933, 505; 1935, 980); at −3° to −8° no (I) results. The structure of (I) follows from pyrolysis at 160—180° to $(CPh_2$:N·$)_2$ and $COPh_2$, hydrolysis by boiling conc. HCl to $COPh_2$, and hydrogenation (PtO_2, EtOH) to $(CPh_2$:N·$)_2$ (100%). In boiling $CHCl_3$, (II) gives the *substance*, $(CPh_2$:N$)_2O$ (III), m.p. 167°, and CPh_2:N·OH, in boiling C_6H_6 gives (III), CPh_2:N·OH, and $COPh_2$, and in AcOH gives N_2 and equiv. amounts of CPh_2:N·OH and $COPh_2$. At 194°, (II) gives N_2 (64·7%), (III), $(CPh_2$:N·$)_2$, and $COPh_2$. With Bu^{α}_2O–MgPhBr, (II) gives N_2 (68%), (III), CPh_3·OH, and a little PhOH; with MgMeI, CPh_2Me·OH is obtained. (II) is stable to NaOMe, NaOEt, and Na–Hg–EtOH–C_6H_6. AcOH containing a little Ac_2O hydrolyses (III) to CPh_2:N·OH (90%). R. S. C.

Grignard reactions involving the benzene nucleus. R. C. Fuson, M. D. Armstrong, and S. B. Speck (*J. Org. Chem.*, 1942, **7**, 297—302).—Benzoylmesitylene (I) condenses with MgPhBr in the 1 : 4 manner to the conjugated system formed by CO and a double linking of the Ph group. (I) and MgPhBr in dry Et_2O give mainly *o-phenylbenzoylmesitylene* (II), m.p. 89—90°, accompanied by Ph_2, unchanged material, a white *compound* (III), $C_{22}H_{22}O_2$, m.p. 245—246° [*acetate*, m.p. 101° (corr.)], and tar. (II) is degraded by syrupy H_3PO_4 to *o*-C_6H_4Ph·CO_2H. (II) is obtained synthetically from 2 : 4 : 6 : 1-$C_6H_2Me_3$·COCl and *o*-C_6H_4Ph·MgI. Oxidation of the enol intermediate obtained from (I) and MgPhBr gives some (III). 1-Naphthoylmesitylene and MgPhBr give a tar from which 2 : 1-$C_{10}H_6Ph$·OH, m.p. 210—211°, mesitoic acid, and apparently a dinaphthone, m.p. >220°, are isolated. *p*-C_6H_4Br·COCl, *s*-$C_6H_3Me_3$, and $AlCl_3$ in Cl_2 yield p-*bromobenzoylmesitylene* (IV), m.p. 72—73° (corr.), converted by MgPhBr into a *compound* (IV), $C_{22}H_{21}OBr$, m.p. 121° (corr.), and a yellow *isomeride*, m.p. 131° (corr.). (IV) does not give a ppt. with $AgNO_3$ in EtOH. It could not be acetylated, reduced, or dehydrogenated. It does not condense with $(CH_2$·$CO)_2O$ and does not contain active H. When brominated in AcOH it gives the *substance*, $C_{22}H_{19}OBr_5$, m.p. 175° (corr.). 1-$C_{10}H_7$·MgBr and (IV) give isomeric *compounds*, $C_{26}H_{23}OBr$, m.p. 195° (corr.) and 143° (corr.). 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO·C_6H_4Me-*p* and *p*-C_6H_4Me·MgBr give, *inter alia*, 2-*mesitoyl*-5 : 4′-*dimethyldiphenyl*, m.p. 101° (corr.). H. W.

Difficultly reactive carbonyl groups. W. Dilthey and W. Schneider-Windmüller (*J. pr. Chem.*, 1942, [ii], **159**, 273—291).—The reactivity of CO in compounds C_6H_4R·CO·CHPh·CHPh·CO·C_6H_4R' and allied types is studied by oximation, reduction to cyclic substances, and salt formation and the observed steric hindrance is explained by the theory of induced polarities. *aε-Diketo-aβγ-triphenyl*-ε-p-*bromophenylpentane*, m.p. 235—237°, loses Br when reduced by Zn dust and AcOH, yields a *salt*, $C_{29}H_{20}OCl_4BrFe$, m.p. 235° (with anhyd. $FeCl_3$ in Ac_2O), and a *mono-oxime*, m.p. 237°.
p-CHPh:N·C_6H_4·CO·CH:CHPh, m.p. 154° (lit. 143—144°), and CH_2PhBz in C_5H_5N containing NaOMe afford *aε-diketo-aβγ-triphenyl*-ε-p-*benzylideneaminophenylpentane*, m.p. 218—219°, which is hydrolysed (HCl–MeOH) to the *NH_2-diketone*, m.p. 237° (*Bz* derivative, m.p. 248°); these compounds give resins when treated with Zn and AcOH. *p*-OH·C_6H_4·$CO·CH_2Ph$ (I), m.p. 146—147° [lit. 142° (corr.)], does not give a red colour with alkali and is not smoothly reduced; its acetate, m.p. 85—86°, is reduced to *βγ-dihydroxy-aδ-diphenyl-βγ-di*-p-*acetoxyphenylbutane*, m.p. 206—207°, with an unidentified by-product, m.p. 148°. (I), CH_2O, and KOH in aq. MeOH yield aε-diketo-βδ-diphenyl-aε-di-*p*-hydroxyphenylpentane, m.p. 161—163°; the *diacetate*, m.p. 176—177°, is reduced to the corresponding *pinacol*, $C_{33}H_{30}O_2$, m.p. 204—205°. *aε-Diketo-βγε-triphenyl*-α-p-*hydroxyphenylpentane*, m.p. 203—204°, and its *acetate*, m.p. 191°, could not be reduced satisfactorily. *aε-Diketo-βγε-triphenyl*-α-p-*anisylpentane*, m.p. 188—189°, resists attempted reduction and is converted by a large excess of NH_2OH into a *mono-oxime*, m.p. 232°. *aε-Diketo-βγ-diphenyl-aε-di*-p-*anisylpentane*, m.p. 203—204°, is very resistant to oximation and reduction whereas *aε-diketo-βε-diphenyl-αγ-di*-p-*anisylpentane*, m.p. 163—164°, affords a *mono-oxime*, m.p. 190°, but is not reduced by Zn dust–AcOH or by Al–Hg in EtOH. *aε-Diketo-βγε-triphenyl*-α-p-*tolylpentane*, m.p. 190°, gives a *mono-oxime*, m.p. 222—223°, but is not reduced whilst *aε-diketo-βγ-diphenyl*-α-p-*tolyl*-ε-p-*anisylpentane*, m.p. 193—194°, does not react with NH_2OH or Zn–AcOH. (I), PhCHO, and piperidine at room temp. give the unstable piperidinobenzylidene-*p*-hydroxydeoxybenzoin, m.p. 155—157°, which passes in boiling AcOH into *benzylidene*-p-*hydroxydeoxybenzoin*, m.p. 191—192° (*acetate*, m.p. 122—123°), reduced by Zn dust and AcOH to *benzyl*-p-*hydroxydeoxybenzoin*, m.p. 196—198°. *Benzylidene*-, m.p. 90—91°, and *benzyl*- (II), m.p. 101—102°, -p-*methoxydeoxybenzoin* are obtained analogously. (II) is also obtained from *p*-OMe·C_6H_4·$CO·CH_2Ph$, CH_2PhCl, and powdered KOH. *Anisylidene*-p-*hydroxydeoxybenzoin* has m.p. 171—172° (possibly a second *form*, m.p. 183—184°). aε-Diketo-γ-phenyl-aε-di-*p*-tolylpentane, m.p. 115°, affords a *dioxime*, m.p. 186°, and is reduced by Zn dust–AcOH to 5-*phenyl*-2 : 3-*di*-p-*tolyl*-$\Delta^{2:4}$-cyclo*pentadiene*, m.p. 100—101° H. W.

Bromo-derivatives of aδ-dimesitylbutane-aβδ-trione enol. R. E. Lutz and D. H. Terry (*J. Org. Chem.*, 1942, **7**, 274—279).—Dimesitylbutanetrione enol (I) is converted by Br (1 equiv.) in CCl_4 at 0° followed by treatment of the product with conc. AcOH at 60° into *γ-bromo-aδ-dimesitylbutane-aβδ-trione*, m.p. 105·5—106°, which gives a pale red colour with $FeCl_3$–EtOH which deepens on keeping. It is reduced by SO_2 in EtOH or by KI in conc. AcOH to (I). Br in $CHCl_3$ and (I) at 15° afford *γ-bromo-aδ-dimesitylbutane-aβδ-trione enol* (II), m.p. 106·5—107·5°, which gives a dark red colour with $FeCl_3$ in EtOH, is sol. in aq. NaOH or Na_2CO_3, and gives a Na, m.p. 206—209°, and Ag salt. (II) and CH_2N_2 in Et_2O afford *γ-bromo-β-methoxy-aδ-dimesityl-Δβ-butene-aδ-dione* (III), m.p. 125·5—126°, hydrolysed by conc. AcOH containing H_2SO_4 to (II) but stable towards KI in conc. AcOH at 70°. This is catalytically reduced (PtO_2 in EtOH) to β-methoxy-aδ-dimesitylbutane-aδ-dione. (III) is unaffected by sunlight. Ozonolysis of (III) gives mesitylglyoxylic and mesitoic acid. The residues from the prep. of (III) afford an isomeric *Me ether*, m.p. 156—156·5°. (I) and Br (2 equivs.) in EtOH at −10° yield *γγ-dibromo-aδ-dimesitylbutane-aβδ-trione*, m.p. 152—152·5°, whilst (I) and $PhICl_2$ in $CHCl_3$ at room temp. give a *compound*, $C_{22}H_{21}O_3Cl_3$, m.p. 142—142·5°. H. W.

Acylation of aδ-dimesitylbutane-aβδ-trione enol. R. E. Lutz and D. H. Terry (*J. Amer. Chem. Soc.*, 1942, **64**, 1375—1377).—Acylation of aδ-dimesitylbutane-aβδ-trione enol (I) gives *O*-acyl derivatives (cf. the Ph_2-trione, A., 1936, 1524; 1939, II, 375). The Na enolate with BzCl in boiling Pr^{β}_2O or 10% NaOH at room temp. gives 60 or 24%, respectively, of *β-O*-benzoate (II), m.p. 141—141·5°, hydrolysed by boiling HCl–AcOH–H_2O to (I) and hydrogenated (PtO_2; EtOH) to OH·CR:C(OBz)·CH:CR·OH (here and below R = mesityl) (not isolated), which when kept gives *β-benzoyloxy-aδ-dimesitylbutane-aδ-dione* (III), m.p. 153·5—154°, or with piperidine (2 drops) gives $(CH·COR)_2$ (IV) (65%) + BzOH, or with I regenerates (II). With O_3 in $CHCl_3$ at 0°, (II) gives $RCO·CO_2H$ (43%), RCO_2H (31%), and BzOH (56%). HCl–AcOH–H_2O hydrolyses (III) to $RCO·CH(OH)·CH_2·COR$ (V) and (I). BzCl and $[COR·CH(OH)·]_2$ (VI) give *βγ-dibenzoyloxy-aδ-dimesitylbutane-aδ-dione*, m.p. 162° [and some (II)], which with boiling BzCl gives a substance, m.p. 180—182°, and is hydrolysed to (II). 5% NaOH–MeOH at 60—70° converts (VI) into (I) (65%). BzCl and (V) give only (IV). The Na enolate of (I) with boiling AcCl–Pr^{β}_2O or the Ag enolate with AcCl–abs. EtOH at 0°—room temp. gives 72 or 35%, respectively, of the *β-O*-acetate (VII), m.p. 144°, hydrolysed to (I); similarly, (VI) and Ac_2O–H_2SO_4 at 0° and later 70° give the *βγ*-diacetate, m.p. 181°, stable to BzCl and hydrolysed by NaOMe at room temp. to (I) or by acid to (VII). R. S. C.

Reduction of *cis*- and *trans*-β-enol methyl ethers of aδ-dimesitylbutane-aβδ-trione. R. E. Lutz and D. H. Terry (*J. Org. Chem.*, 1942, **7**, 280—285).—Reduction ($Na_2S_2O_4$) of *cis*- (I) and *trans*- (II) -β-methoxy-aδ-dimesityl-Δβ-butene-aδ-dione proceeds similarly in each case giving β-methoxy-aδ-dimesitylbutane-aδ-dione (III) and, mainly, the fission products, mesitoic acid and acetylmesitylene. (I) gives a small amount of mesitylglyoxal hydrate (III) whilst (II) gives a small amount of an unidentified compound. Dimesityl-

butanedione (V) is not formed. Dimesitylbutanetrione enol is reduced ($Na_2S_2O_4$) to a small quantity of αδ-dimcsitylbutane-αδ-dion-β-ol, a large amount of δ-hydroxy-αδ-dimesitylbutane-αγ-dione enol, and a trace of (IV); cleavage is relatively small. Catalytic reduction of (II) affords 65% of (III) and 25% of (V) whereas (V) is obtained almost quantitatively from (I). The mechanism of the reactions is described. H. W.

Phenol–formaldehyde resins. IV. Influence of substituents on the polymerisation of *o*-quinonemethides. K. Hultzsch (*J. pr. Chem.*, 1941, [ii], **159**, 180—188).—Polymeric quinonemethides are obtained by shaking 1 : 4 : 2 : 6-OH·C_6H_2R(CH_2Cl)$_2$ (I) [from OH·C_6H_2R(CH_2·OH)$_2$ and AcOH–HCl] with aq. Na_2CO_3 in Et_2O. *4-tert.*-Butyl-2 : 6-di(chloromethyl)phenol, m.p. 68°, thus affords trimeric 5-tert.-*butyl-3-chloromethyl-2-quinonemethide*, m.p. 175°; (I) (R = Me) yields trimeric *5-methyl-3-chloromethyl-2-quinonemethide*, m.p. 163°; *4-αayy-tetramethylbutyl-2 : 6-di(chloromethyl)phenol*, m.p. 87°, gives polymeric *5-αayy-tetramethylbutyl-3-chloromethyl-2-quinonemethide*, amorphous (*M* 1065, 1515; Cl 10·47, 9·04%). C. S.

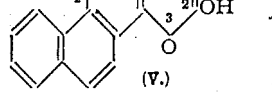
Tetrahydroresorcinol [3-hydroxy*cyclo*hexanone]. K. Dimroth and K. Resin (*Ber.*, 1942, **75**, [*B*], 322—326).—*m*-$C_6H_4(OH)_2$ is hydrogenated (Ni in EtOH) at 150—160° (max.) to *cyclo*hexane-1 : 3-diol (I), partly esterified (BzCl in $CHCl_3$) to the benzoate (II), which is treated with 3 : 5 : 1-$(NO_2)_2C_6H_3$·COCl in C_5H_5N and then separated by crystallisation followed by chromatography into cis-, m.p. 169°, and trans-, m.p. 123—124°, -*cyclohexane*-1 : 3-*diol benzoate* 3 : 5-*dinitrobenzoate*. (II) is oxidised by CrO_3 in cold AcOH to 3-*keto*cyclo*hexyl benzoate*, m.p. 61—62° (2 : 4-*dinitrophenylhydrazone*, m.p. 146—148°), which readily loses BzOH when heated, with formation of Δ²-*cyclo*hexenone (2 : 4-*dinitrophenylhydrazone*, m.p. 167·5—169°). Partial acetylation of (I) by AcCl in boiling $CHCl_3$ gives the *monoacetate*, b.p. 131—132·5°/13 mm. (62%), oxidised to 3-*keto*cyclo*hexyl acetate*, b.p. 116—118°/11·5 mm., readily hydrolysed by 3% NaOH at room temp. to tetrahydroresorcinol, b.p. 95°/1 mm. H. W.

Attempted synthesis of the antirachitic vitamin. VII. Preliminary experiments on the introduction of the hydroxyl group into ring A. K. Dimroth and E. Stockstrom (*Ber.*, 1942, **75**, [*B*], 326—331).—*cyclo*Hexanone, NH_2Me_2Cl, and 33·3% CH_2O condense in amyl alcohol, decahydronaphthalene, or, best, CH_2Ph·OH to 2-dimethylaminomethyl*cyclo*hexanone and a *compound*, $C_{10}H_{22}O_3NCl$, m.p. 98° (corresponding *picrate*, $C_{16}H_{22}O_9N_4$, m.p. 147—148°). Similarly 3-keto*cyclo*hexyl acetate gives α- (I), m.p. 154°, and β- (II), m.p. 92°, -3-*keto-2-dimethylaminomethyl*cyclo*hexyl acetate hydrochloride* and α- (III), m.p. 191°, and β- (IV), m.p. 165°, -3-*keto-4-dimethylaminomethyl*cyclo*hexyl acetate hydrochloride*. The free bases cannot be distilled unchanged but are obtained as oils by the action of 30% KOH and immediate extraction with Et_2O. (III) is thus transformed into the corresponding *picrate*, m.p. 133—134°. The β-compounds are isomerised by HCl in Ac_2O at 100° to the corresponding α-derivatives. (III) and (IV) are converted by the successive action of 30% KOH at room temp. and MgMeI in Et_2O followed by an excess of MeI and heating of the product with Pt at 100—110° into *o*-4-xylenol (3 : 5-*dinitrobenzoate*, m.p. 182°); (I) and (II) are converted similarly into *o*-3-xylenol. H. W.

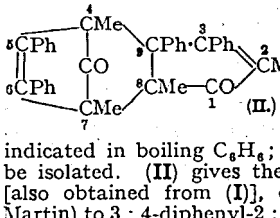
2-*cyclo*Hexylidene*cyclo*hexanone, an isomeride of 2-Δ¹-*cyclo*hexenyl*cyclo*hexanone. J. Reese (*Ber.*, 1942, **75**, [*B*], 384—394).—Wallach's liquid ketone is shown to be 2-Δ¹-*cyclo*hexenyl*cyclo*hexanone (I) and an isomeride, 2-cyclo*hexylidene*cyclo*hexanone* (II) is described. 2-1′-Chloro*cyclo*hexyl*cyclo*hexanone in Et_2O is converted by NaOMe in well-cooled MeOH into (II), b.p. 105°/2 mm., m.p. 57°, which gives a *semicarbazone*, softens at 178°, m.p. 180°, re-solidifies at 183°, and melts at 186—188° (decomp.), with an unidentified, non-cryst. material. Optical data support the constitutions assigned to (I) and (II). Titration of (II) with BzO_2H gives the *oxidoketone* (III), $C_{12}H_{18}O_2$, m.p. 98°. (II) is hydrogenated (PtO_2 in EtOAc) to 2-*cyclo*hexyl*cyclo*hexanone. Gentle oxidation ($KMnO_4$) of (II) gives adipic acid (IV) in good yield with a small amount of *cyclo*hexanone (V); under like treatment (I) yields resinous acids, a little (IV), but no (V). (II) and alkaline H_2O_2 afford (III), which does not give a semicarbazone; it is hydrogenated to the *oxido-alcohol*, m.p. ~94°, re-oxidised to (III). Distillation of (III) is accompanied by isomerisation to a *spiro*diketone, $C_{12}H_{18}O_2$ (*semicarbazone*, m.p. 224°). By H_2O_2 with sufficient alkali (I) is converted into ε-*hydroxy*-ε-Δ¹-cyclo*hexenylhexoic acid* (VI), m.p. 70°, with a small proportion of (III). (VI) is reduced (H_2–PtO_2–EtOAc) to ε-*hydroxy*-, m.p. 41°, oxidised (CrO_3 in AcOH at room temp.) to ε-keto-ε-*cyclo*hexylhexoic acid, m.p. 57—58° (semicarbazone, new m.p. 176—177°). Distillation of (VI) under 2 mm. gives ε-Δ¹-cyclo*hexenyl*-Δ⁵-*hexenoic acid*, b.p. 173—180°/2 mm., hydrogenated (PtO_2 in EtOAc) to ε-*cyclo*hexylhexoic acid. (II) is stable at 100° but is partly isomerised to (I) at 150°. 2-1′-Chloro-3′-methyl*cyclo*hexyl-3-methyl*cyclo*hexanone is transformed by NaOMe in MeOH at 0° into 2-3′-*methyl*cyclo*hexylidene*-3-*methyl*cyclo*hexanone*, m.p. 71° (*semicarbazone*, m.p. 171°). H. W.

Syntheses with β-chloroethyl-ketones. J. Décombe (*Compt. rend.*, 1941, **213**, 579—581).—*cyclo*Hexanone, CH_2O, and K_2CO_3 yield >30% of 2-hydroxymethyl-, b.p. 164—165°/12 mm. (*phenylhydrazone*, m.p. 132°), and then (cold HCl–Et_2O) 2-chloromethyl-*cyclo*hexanone, which with CHNaAc·CO_2Et gives *Et α-acetyl-β-2-keto*-cyclo*hexyl propionate*, m.p. 145—146°, hydrolysed (cold KOH) to the 3-CO_2H-derivative (loses CO_2 at 100°) of 2-keto-Δ¹·⁹-octahydronaphthalene, b.p. 137°/14 mm. (Mannich *et al.*, A., 1937, II, 153). Cl·$[CH_2]_2$·COMe (I) and sodio-2-methyl*cyclo*hexanone afford a product hydrolysed (KOH–EtOH) to 10% of 2-*keto*-10-*methyl*-Δ¹·⁹-*octahydronaphthalene*, b.p. 142—148°/14 mm. (*semicarbazone*, m.p. 220—225°). (I) and sodio-2-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (or better its Et carbonate) afford 2-ketohexahydrophenanthrene, m.p. 80° (*loc. cit.*). W. C. J. R.

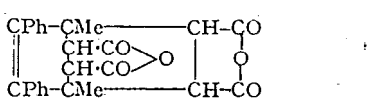
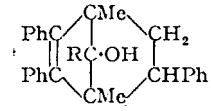
Synthesis of 2′-ketodihydro-1 : 2-*cyclo*pentenophenanthrene and derivatives of phenanthro[1, 2-*b*]furan. A. L. Wilds (*J. Amer. Chem. Soc.*, 1942, **64**, 1421—1429).—2-Bromo-1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (I) (prep. starting from α-$C_{10}H_7$·$[CH_2]_2$·OH improved), m.p. 87—88° (lit. 84—85°), and CHAcNa·CO_2Et in C_6H_6–EtOH give *Et* 1-*keto*-1 : 2 : 3 : 4-*tetrahydro*-2-*phenanthrylacetoacetate* (II) (77%), m.p. partly 108—112°, partly 130—135° (with, in one experiment, a *substance*, m.p. 138—141°), which with 5% KOH at 80° and later 115° (N_2) gives 16-*keto*-11 : 12 : 13 : 17-*tetrahydro*-Δ¹⁴·¹⁵-cyclo*pentenophenanthrene* (III) (numbering as for cholane) (84%), m.p. 185—185·5° [*oxime*, m.p. 247—250° (decomp.) [and 13% of 1-*keto*-1 : 2 : 3 : 4-*tetrahydro*-2-*phenanthrylacetic acid* (IV), m.p. 187·5—188·5° (*Me* ester, m.p. 106—106·5°)]. Zn–Hg–HCl–AcOH–PhMe reduces (III) to an oil, which with Pd–C–N_2 at 300—320° gives 1 : 2-*cyclo*pentenophenanthrene. H_2–Pd–C in dioxan reduces (III) to 16-*keto*-11 : 12 : 13 : 14-*tetrahydrocyclopentanophenanthrene* (91%), *forms*, m.p. 115—116° and 146—147·5° (mixed *oximes*, sinter at 155°, m.p. 163—168°). NaOMe–MeOH converts (II) into 2-*hydroxy*-1-*acetyl*-10 : 11-*dihydrophenanthro*[1, 2-b]*furan* (V) (84%), m.p. 220—223° (decomp.), stable to alkali [also obtained by NaOEt–EtOH without isolation of (II)], or, in one experiment, 2-*methyl*-10 : 11-*dihydrophenanthro*[1, 2-b]-*furan*-1-*carboxylic acid* (VI) (30%), m.p. 328—331° (block) [*Me* ester, m.p. 121·5—122·5°, and *Et* ester (VII), *forms*, m.p. 88·5—90° and 78—80°, also obtained from (V) by HCl–EtOH]. With boiling AcOH–conc. HCl, (II) gives first (V) and then 1-*keto*-2-*acetonyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (80%), m.p. 97—98°. Pd–C–N_2 at 200—210° dehydrogenates (VII) to *Et* 2-*methylphenanthro*[1, 2-b]*furan*-1-*carboxylate* (92%), m.p. (bath preheated at 110°) 116·5—124° or (bath preheated at 120°) 123·5—124° after melting and resolidification (corresponding *Me* ester, m.p. 142·5—144°, similarly prepared), and thence (KOH–MeOH–H_2O) the *acid* (VIII), m.p. 323—325° (block). Cu chromite in boiling quinoline decarboxylates (VI) to 2-*methyl*-10 : 11-*dihydrophenanthro*[1, 2-b]*furan* (69%), m.p. 72—74°, and (VIII) to 2-*methylphenanthro*[1, 2-b]*furan* (67%), m.p. 112—112·5°. CHNa(CO_2Et)$_2$ and (I) in C_6H_6–EtOH followed by EtOH–NaOEt give *Et* 2-*hydroxy*-10 : 11-*dihydrophenanthro*[1, 2-b]*furan*-1-*carboxylate* (IX) (60%), m.p. 126—127·5° [and a little of a *substance*, $C_{22}H_{20}O_5$, m.p. 220—222° (decomp.)]; hydrolysis and decarboxylation in boiling H_2O (or at 180°) of the malonate yields (IV) (73—84%), reduced (Clemmensen–Martin) to 1 : 2 : 3 : 4-*tetrahydro*-2-*phenanthrylacetic acid* (84—89%), m.p. 167—168°. The derived *Me* ester, m.p. 67—68°, is dehydrogenated (Pd–C; 240—250°) to Me 2-phenanthrylacetate (X), m.p. 78·5—79° (lit. 78—78·5°) [derived acid, m.p. 194·5—195·5° (lit. 183·5—184·5°, ? another form). When distilled (0·5 mm.) (79%) or boiled in AcOH (74%), (V) gives 2-*phenanthrylacetone* (XI), m.p. 91—91·5° (*oxime*, m.p. 197—198°) [(IX) gives mixtures by these methods], reduced (Clemmensen–Martin) to 2-*n*-propylphenanthrene [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 102·5—103·5°]. MgMeI with (X) or (XI) gives 2-*phenanthryl*-tert.-*butyl alcohol*, m.p. 119·5—120°. Al(OPr^β)$_3$–Pr^βOH and (XI) give *β-2-phenanthrylisopropyl alcohol*, m.p. 107—107·5°. R. S. C.


(V.)

Carbonyl bridge compounds. C. F. H. Allen and J. Van Allan (*J. Amer. Chem. Soc.*, 1942, **64**, 1260—1267).—Loss of the *endo*-CO from within six-membered rings by heat alone (200°) or in solution occurs only by the fission, C:C·C·CO → C:C·C + CO, and only when it is necessary for formation of an aromatic ring; in other respects the CO behaves normally. The bimol. product from 4-hydroxy-3 : 4-diphenyl-2 : 5-dimethyl-Δ²-*cyclo*pentenone [αβ-dimethylanhydroacetonebenzil] (I) (Gray, *J.C.S.*, 1909, **95**, 2134) is 4 : 7-endo*keto*-3 : 5 : 6 : 9-*tetraphenyl*-2 : 4 : 7 : 8-*tetramethyl*-4 : 7 : 8 : 9-*tetrahydroinden*-1-*one* (II) (cf. the unmethylated homologue, A., 1933, 1164). (II) reacts largely as the monomeric 3 : 4-diphenyl-2 : 5-dimethyl*cyclo*pentadienone (III). Solid (II) is colourless, but the solution is red in hot solvents, 20% dissociation being indicated in boiling C_6H_6; no coloured substance could, however, be isolated. (II) gives the 2 : 4-*dinitrophenylhydrazone*, m.p. 242° [also obtained from (I)], of (III) and is reduced (Clemmensen–Martin) to 3 : 4-diphenyl-2 : 5-dimethyl*cyclo*pentanone. Reacting as (III), (II) adds as diene in the Diels–Alder reaction: thus with CHPh:CH_2 it gives 3 : 6-endo*keto*-1 : 2 : 4-*triphenyl*-3 : 6-*dimethyl*-Δ¹-cyclo*hexene* (IV) (90%), m.p. 131°; with CHPh:CH·NO_2 it gives


(II.)

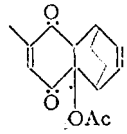
5-*nitro*-3 : 6-endo*keto*-1 : 2 : 4-*triphenyl*-3 : 6-*dimethyl*-Δ^1-cyclo*hexene* (**V**) (91%), m.p. 176° (5-*Br*-derivative, m.p. 148°, formed by Br–NaOEt–EtOH–C_6H_6); with $(CH{\cdot}CO)_2O$ it gives 3 : 6-endo*keto*-4 : 5-*diphenyl*-3 : 6-*dimethyl*-Δ^4-*tetrahydrophthalic anhydride* (**VI**) (99%), m.p. 191°, or with an excess the *substance* (**VII**) (95%), m.p. 320° [also obtained from (**VI**)], which are also obtained from (**I**) in

(VII.)  (XV.) 

presence of a drop of H_2SO_4; with $COPh{\cdot}CH{:}CH_2$ it gives 3 : 6-endo*keto*-4-*benzoyl*-1 : 2-*diphenyl*-3 : 6-*dimethyl*-Δ^1-cyclo*hexene* (**VIII**) (77%), m.p. 147°; with C_2H_2 it gives, with loss of CO, 2 : 3-*diphenyl*-p-*xylene* (**IX**) (51%), m.p. 109°; with $CPh{:}CH$ it gives similarly *triphenyl*-p-*xylene* (**X**) (90%), m.p. 157°; with Me_2 maleate or fumarate it gives *Me*$_2$ 3 : 6-endo*keto*-4 : 5-*diphenyl*-3 : 6-*dimethyl*-Δ^4-*tetrahydro*-trans- (**XI**) (83%), m.p. 144°, and -cis-*phthalate* (**XII**) (73%), m.p. 128°, respectively; with Et_2 maleate it gives, with loss of CO, *Et*$_2$ 4 : 5-*diphenyl*-3 : 6-*dimethyl*-1 : 2-*dihydrophthalate* (64%), b.p. 210—213°/3 mm.; with $(CO{\cdot}CO_2R)_2$ it gives, with loss of CO, *Me*$_2$ (**XIII**) (90%), m.p. 212°, and *Et*$_2$ 4 : 5-*diphenyl*-3 : 6-*dimethylphthalate* (81%), m.p. 132°; with $CH_2{:}CH{\cdot}CO_2Me$ it gives *Me* 2 : 5-endo*keto*-3 : 4-*diphenyl*-2 : 5-*dimethyl*-Δ^3-*tetrahydrobenzoate* (**XIV**) (92%), m.p. 115°; with $CHEt{:}CH{\cdot}CO_2H$ it gives 2 : 5-endo*keto*-3 : 4-*diphenyl*-2 : 5-*dimethyl*-6-*ethyl*-Δ^3-*tetrahydrobenzoic acid* (75%), m.p. 188°. With Br in CCl_4 or $CHCl_3$, (**I**) or (**II**) gives HBr and a *substance*, $C_{38}H_{32}O_2Br_6$, m.p. 136° (decomp.). At 200° (**IV**) gives CO and 2 : 3 : 5-triphenyl-5 : 6-dihydro-*p*-xylene, readily dehydrogenated by Br–$CHCl_3$ to (**X**), which is obtained directly (loss of CO and HNO_2) from (**V**). The CO of (**IV**) is not sterically hindered : it gives readily a 2 : 4-*dinitrophenylhydrazone*, m.p. 200°; with MgMeI it shows 1 active H and no addition; with MgRX (" forced ") it gives *carbinols* (**XV**) (89—93%), R = *Me*, m.p. 119°, *Ph*, +*x*AcOH, m.p. 107° (decomp.) (with AcCl gives the *chloride*, m.p. 128°), and α-$C_{10}H_7$, m.p. 98°. At 200° (**VI**) gives 4 : 5-*diphenyl*-3 : 6-*dimethyl*-1 : 2-*dihydrophthalic anhydride*, m.p. 158° [obtained also when an attempt is made to prepare (**VII**) in $C_6H_3Cl_3$], which with $(CH{\cdot}CO)_2O$ gives (**VII**) and is dehydrogenated (Br, KOH–EtOH) to 4 : 5-*diphenyl*-3 : 6-*dimethylphthalic anhydride* (**XVI**), m.p. 281°, converted into (**IX**) by distillation with soda-lime. At 200° (**VIII**) loses CO and 2 H, giving 3 : 4-*diphenyl*-2 : 5-*dimethylbenzophenone*, m.p. 160°; with $NaNH_2$ this gives (**IX**) and with MgMeI (" forced ") gives 2 : 3-*diphenyl*-6-*a*-*phenylvinyl*-p-*xylene* (90%), m.p. 151°, whence it is regenerated by oxidation. (**IX**) is also formed by heating (**VII**) with $Ba(OH)_2$, one mol. of $(CH{\cdot}CO)_2O$ being eliminated. At 200° (**XI**) and (**XII**) give *Me*$_2$ trans- (**XVII**) (86%), m.p. 131°, and cis-4 : 5-*diphenyl*-3 : 6-*dimethyl*-1 : 2-*dihydrophthalate* (**XVIII**) (99%), b.p. 197—200°/2 mm., both dehydrogenated by $KMnO_4$ in boiling $COMe_2$ to (**XIII**) and converted by 100% H_2SO_4 into (**XVI**), which is also obtained from (**XIII**) by KOH–EtOH and from (**XVIII**) by Br, followed by KOH–EtOH. With Br, (**XVII**) gives *Me*$_2$ 1 : 2 : 3 : 6-*tetrabromo*-4 : 5-*diphenyl*-3 : 6-*dimethyl*-Δ^4-*tetrahydrophthalate*, m.p. 181, converted into (**XVI**) by KOH–EtOH. Heating (**XIV**) and subsequently oxidising ($KMnO_4$) gives *Me* 3 : 4-*diphenyl*-2 : 5-*dimethylbenzoate*, m.p. 116°, which is also obtained as a by-product during one prep. of (**XI**). With MgRBr (" forced "), (**II**) gives 4 : 7-endo*keto*-1 : 3 : 5 : 6 : 9-*pentaphenyl*-2 : 4 : 7 : 8-*tetramethyl*-, m.p. 223°, and 4 : 7-endo*keto*-3 : 5 : 6 : 9-*tetraphenyl*-1 : 2 : 4 : 7 : 8-*pentamethyl*-, m.p. 205°, -4 : 7 : 8 : 9-*tetrahydroinden*-1-*ol*. R. S. C.

Dehydroechinochrome. R. Kuhn and K. Wallenfels (*Ber.*, 1942, **75**, [*B*], 407—413).—Echinochrome (**I**) is converted by Ag_2O in dry Et_2O or by aq. HOCl at 0—5° into *dehydrocchinochrome* (**II**) (+H_2O), softens at 70°, decomp. 90—100°, or (+2H_2O) decomp. 160—165°. Conversion of (**I**) into its leuco-compound and dehydrogenation of it to (**II**) are reversible processes occurring in potential ranges corresponding with those of known dehydrogenase systems. (**II**) is reduced to (**I**) by fermenting yeast. Absorption spectrum, solubility, formation of hydrates, and behaviour towards reducing agents indicate that (**II**) is not a substituted naphtha-1 : 4 : 5 : 8-diquinone but a derivative of 1 : 2 : 3 : 4-tetraketotetrahydronaphthalene. 2 : 3-Dihydroxynaphthazarin is oxidised by Ag_2O to 5 : 8-*dihydroxy*-1 : 2 : 3 : 4-*tetraketotetrahydronaphthalene* (**III**) (+H_2O), m.p. ~175° (decomp.), which resembles (**II**) in absorption spectrum, ability to form hydrates, sp. behaviour towards H_2S, and in solubility. (**II**) and (**III**) differ in absorption spectrum from 2-methylnaphtha-1 : 4-5 : 8-diquinone. Also, the undoubted 1 : 2 : 3 : 4-tetraketotetrahydronaphthalene resembles (**II**) and (**III**) in very many of its properties and shows marked differences from the isomeric naphtha-1 : 4-5 : 8-diquinone. (**II**) is undoubtedly 5 : 6 : 8-*trihydroxy*-1 : 2 : 3 : 4-*tetraketo*-7-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. H. W.

Synthesis of condensed ring compounds. IX. Reaction of 4-acetoxy-*p*-tolu-2 : 5-quinone with conjugated dienes and the rules of Alder. E. W. J. Butz and L. W. Butz (*J. Org. Chem.*, 1942, **7**, 199—226).—The dienes react with the OAc·C:C linking of the quinone to an equal or greater extent than with the CMe:C linking. Hexatriene and 2 : 1 : 4 : 5-O:C_6HMe(OAc):O (**I**) in EtOH and CO_2 at 70° or 95° give the following compounds : (*A*) 1 : 4-*diketo*-9-*acetoxy*-3-*methyl*-5(or 8)-*vinyl*-5 : 8 : 9 : 10-*tetrahydronaphthalene* (**II**), m.p. 109—110°, in 45% yield; (*B*) a colourless *compound* (**III**), $C_{13}H_{14}O_3$, m.p. 206—210° after decomp. at 195°, and (*C*) a small amount of a *substance* (**IV**), $C_{15}H_{16}O_4$, m.p. (indef.) 135—140°, isolated on a single occasion. (**II**) does not give a colour with $FeCl_3$ and could not be hydrolysed to a product giving such a colour; at 200—215°/80 mm. it gives AcOH and unidentified tarry matter. (**III**) dissolves in cold dil. aq. NaOH and can be repptd. unchanged by HCl from the solution. It gives a purple-black to brown-black solution with $FeCl_3$. The relatively high temp. of decomp. indicates the possibility that (**III**) is a dienol. (**IV**) gives a green solution with $FeCl_3$. It is decomposed by hot H_2O with formation of (**III**). The identity of the compound, $C_{15}H_{16}O_4$ (A., 1938, II, 104), is in doubt. At 65°, (**I**) and *cyclo*hexadiene yield (*D*) a *substance* (**V**), $C_{15}H_{16}O_4$, m.p. 123—124°, obtained in 55% yield, (*E*) a *compound*, (**VI**), $C_{13}H_{14}O_3$, m.p. 152—153°, and (*F*) 6% of a *substance* (**VII**) $C_{15}H_{16}O_4$, m.p. 84—87°. (**V**) is not an enol acetate since it does not give a colour with $FeCl_3$ either before or after attempted hydrolysis. When heated at 210—215° (bath)/100—110 mm. it gives AcOH and 1 : 2 : 4-O:$C_{10}H_5$Me:O (**VIII**) and hence is (*G*). (**VI**) is sol. in dil. aq. NaOH, gives a brown colour with $FeCl_3$, and has evidently been formed by hydrolysis of an enol acetate. (**VII**) cannot be an enol acetate since it does not hydrolyse to an enol but decomposes on heating into AcOH and (**VIII**). Hence (**VII**) and (**V**) are isomeric, the relationship being probably of the *endo–exo* type.


(*G*.)

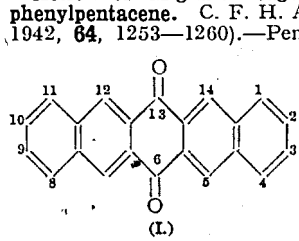
[With A. M. Gaddis.] (**I**) and $(CH_2{:}CMe{\cdot})_2$ in EtOH at 95° afford 1 : 4-*diketo*-9-*acetoxy*-3 : 6 : 7-*trimethyl*-5 : 8 : 9 : 10-*tetrahydronaphthalene*, m.p. 116—117°, in 42% yield. It is not converted into an enol when heated with dil. AcOH. At 210—215°/80—85 mm. it gives AcOH and a cryst. residue from which a quinol (?), m.p. 170—175°, could be isolated and which is oxidised by $FeCl_3$ to 2 : 6 : 7-trimethyl-1 : 4-naphthaquinone in good yield. M.p. are corr.

It is shown that the rules of Alder and Stein can be applied when the max. density of double linkings is determinable by inspection of conventional formulæ drawn to scale and suitably juxtaposed, when the max. density cannot be thus ascertained but can be deduced from measurements of such drawings supported by simple calculations, and in the presence of double linkings in mobile groups; in the last case the position of nearest approach of the mobile double linking to the other double linkings must be determined and the measurements and calculations made as above. H. W.

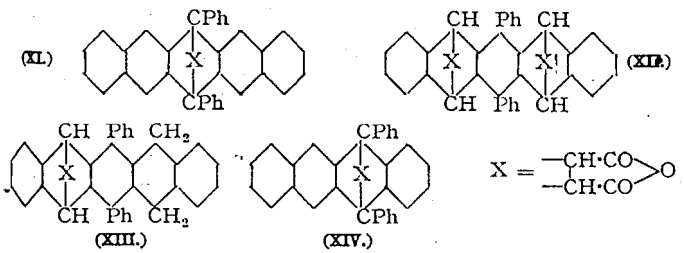
Successive diene addition and dehydrogenation in nitrobenzene solution without isolation of the hydroaromatic intermediate. E. Bergmann, L. Haskelberg, and F. Bergmann (*J. Org. Chem.*, 1942, **7**, 303—306).—In hot $PhNO_2$ $CHPh{:}CH{\cdot}CH{:}CH_2$ with *p*-O:C_6H_4:O (**I**) and 1 : 4-O:$C_{10}H_6$:O (**II**) give respectively 1 : 5-diphenyl-, m.p. 355°, and 1-phenyl-, m.p. 177°, -anthraquinone. Analogously $(CHPh{:}CH{\cdot})_2$ with (**I**) and (**II**) affords 1 : 4 : 5 : 8-tetraphenyl-, m.p. 355°, and 1 : 4-diphenyl-anthraquinone. 3 : 4-*Diphenyl*-6-*methylphthalic anhydride*, m.p. 161°, is obtained from $\alpha\beta$-diphenyl-$\Delta^{\alpha\gamma}$-pentadiene and $(CH{\cdot}CO)_2O$ (**III**) in boiling $PhNO_2$. $\alpha\beta\delta$-Triphenyl-$\Delta^{\alpha\gamma}$-butadiene and (**III**) in $PhNO_2$ at 100° give 3 : 4 : 6-*triphenylphthalic acid* (+H_2O), m.p. 172°. 9-Δ^1-*cyclo*Pentenylphenanthrene and (**III**) in boiling $PhNO_2$ yield 1 : 2-*cyclo*pentenotriphenylene-3 : 4-dicarboxylic anhydride, m.p. 284°. 9-*Methyl*-, m.p. 164°, or 9-*phenyl*-, m.p. 221°, 1—11 : 14-*dodecahydrophenanthrene*-10-*carboxylic acid* are derived, however, from di*cyclo*hexenyl (**IV**) and $CHMe{:}CH{\cdot}CO_2H$ or $CHPh{:}CH{\cdot}CO_2H$, respectively, in boiling $PhNO_2$, whilst (**III**) and (**IV**) analogously give 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene-9 : 10-dicarboxylic anhydride, m.p. 305°. H. W.

Dehydrogenation of echinochrome and other 2 : 3-dihydroxynaphthaquinones by peroxidase and hydrogen peroxide. K. Wallenfels and A. Gauhe (*Ber.*, 1942, **75**, [*B*], 413—424).—Echinochrome (**I**) is not dehydrogenated by H_2O_2 alone but the change occurs rapidly in the presence of peroxidase, best at p_H 4·7; (**I**) is regenerated by passing H_2S into the solution. The change is of the first order and is restricted by increase of $[H_2O_2]$. Examination of many naphthaquinones shows that dehydrogenation does not depend on a corresponding redox potential but on a sp. arrangement of OH groups. Only those compounds with OH at $C_{(2)}$ and $C_{(3)}$ are dehydrogenated. H. W.

Action of Grignard reagents on pentacenequinones. 6 : 13-Diphenylpentacene. C. F. H. Allen and A. Bell (*J. Amer. Chem. Soc.*, 1942, **64**, 1253—1260).—Pentacene-6 : 13-quinone (in conc. H_2SO_4 blue with red fluorescence) has the bond-structure (**I**), since with MgPhBr it behaves as an $\alpha\beta$-unsaturated diketone having a crossed conjugated system : in Et_2O–Bu_2O, later Bu_2O at 100°, it gives, by 1 : 2-addition, trans-6 : 13-*diphenyl*-6 : 13-*dihydropentacene*-6 : 13-*diol* (**II**) (70%), m.p. 315°, and, by 1 : 4-addition, 5 : 14-diphenyl-5 : 5*a* : 13*a* : 14-tetrahydro- (15%), oxidised by air in KOH–EtOH to 5 : 14-*diphenyl*-


(I.)

pentacene-6 : 13-*quinone* (**III**), m.p. 309° (blue in H_2SO_4; unaffected by $Na_2S_2O_4$). The structure of (**III**) is proved by cleavage by KOH at 310° (later 290°) to 1 : 4-$C_{10}H_6Ph_2$, 1 : 4 : 2-$C_{10}H_5Ph_2{\cdot}CO_2H$, and β-$C_{10}H_7{\cdot}CO_2H$. With MgPhBr–Et_2O at room temp., (**III**) gives, by 1 : 4-addition, 5 : 7 : 12 : 14-*tetraphenyl*-5 : 5a : 13a : 14-*tetrahydro*- (60%), forms, m.p. 272° and 266°, converted at 300° by loss of H_2 into 5 : 7 : 12 : 14-*tetraphenylpentacene*-6 : 13-*quinone*, m.p. 397° (with $NaNH_2$ in cymene gives 75% of 1 : 4-$C_{10}H_6Ph_2$) 1 : 2-Addition to (**III**) occurs with LiPh in Et_2O, yielding 5 : 6 : 13 : 14-*tetraphenyl*-6 : 13-*dihydropentacene*-6 : 13-*diol*, m.p. 392° (stable to KI–AcOH). KI reduces (**II**) to 6 : 13-*diphenylpentacene* (**IV**), violet-blue, m.p. 318—320°, which in C_6H_6 (magenta; orange-red fluorescence in ultra-violet light) is stable in the dark but in CS_2 and light gives the 6 : 13-*peroxide*, +0·25CS_2 and solvent-free, m.p. 221—222° (purple at ~208°), reduced by H_2–Raney Ni in dioxan at 100° to the *cis-isomeride* (**V**), m.p. 269—270°, of (**II**). KI–AcOH reduces (**V**) to (**IV**). In H_2SO_4–MeOH at 0°, (**II**) gives the *Me*$_2$ *ether*, m.p. 258°, stable to Na. Boiling AcBr or HBr–AcOH converts (**II**) or (**V**) into 6 : 13-*dibromo*-6 : 13-*diphenyl*-6 : 13-*dihydropentacene*, m.p. (preheated at 200°) 250—252° (decomp.) or (not preheated) >320° after darkening and sintering at 220°, which in boiling $COMe_2$, C_6H_6, or AcOH gives (**IV**) and Br ($CH_2Br{\cdot}COMe$ in $COMe_2$). CrO_3 oxidises (**IV**) in boiling AcOH to 6 : 13-*diphenylpentacene*-5 : 7 : 12 : 14-*diquinone* (**VI**), m.p. 423°, converted by KOH at 290—300° into *p*-$C_6H_4Ph_2$, *o*-$C_6H_4(CO_2H)_2$ (73%), and BzOH (16%), and by MgPhBr–Et_2O–C_6H_6 into 5 : 6 : 7 : 12 : 13 : 14-*hexaphenyl*-5 : 7 : 12 : 14-*tetrahydropentacene*-5 : 7 : 12 : 14-*tetraol*, m.p. 304°, stable to KI–AcOH. With Br in CCl_4, (**IV**) gives 5 : 14-*dibromo*-6 : 13-*diphenyl*-5 : 14-*dihydro*-, m.p. 235° (decomp.), and then 5 : 7 : 12 : 14-*tetrabromo*-6 : 13-*diphenyl*-5 : 7 : 12 : 14-*tetrahydro-pentacene*, m.p. 205° (decomp.), fluorescent, stable in boiling solvents, reduced to (**IV**) by Zn dust in hot C_6H_6, and at > the m.p. giving HBr and an amorphous Br-containing product, m.p. >500°. (**IV**) is not reduced by Na–Hg and does not add Na, but with H_2–Raney Ni in dioxan at 95—100° gives a 7 : 12-H_2- (**VII**), white, m.p. 247—248° (yellow *dioxide*, m.p. 247—248°), and then the 5 : 7 : 12 : 14-H_4- (**VIII**), m.p. 329—331° (not further hydrogenated), and (? 1 : 2 : 3 : 4 : 5 : 14-)H_6- (**IX**), m.p. 252° (stable to H_2), or, in one experiment, the 1 : 4-H_2-derivative (**X**), m.p. 295°; CrO_3 oxidises (**VII**) or (**VIII**) to (**VI**), but (**IX**) or (**X**) gives an amorphous *substance*, $C_{31}H_{25}O_7$, m.p. 167°. With $(CH{\cdot}CO)_2O$ in boiling xylene, (**IV**) gives *adducts* (**XI**), m.p. 335—337°, and (**XII**), m.p. 255° (decomp.) [not formed from (**XI**)];



(**VII**) gives the *adduct* (**XIII**), m.p. 190° (decomp.); (**VIII**) does not react; naphthacene and 5 : 12-diphenylnaphthacene give adducts, m.p. 293—294° (lit. 273—282°) and 331° (**XIV**), respectively. Pentacene-5 : 7 : 12 : 14-diquinone and MgPhBr in Et_2O, later Bu_2O, give 5 : 7 : 12 : 14-*tetraphenyl*-5 : 7 : 12 : 14-*tetrahydropentacene*-5 : 7 : 12 : 14-*tetraol* (76%), m.p. 270°, reduced by KI–AcOH to 5 : 7 : 12 : 14-*tetraphenylpentacene* (**XV**), purple, m.p. 306—308° (*peroxide*, m.p. 250°). Absorption spectra of (**IV**) and (**XV**) are given.
R. S. C.

Ixone, a tetrabenzopyrenequinone. C. Dufraisse and M. Loury (*Compt. rend.*, 1941, **213**, 689—692).—Cyclisation (H_2SO_4) of 6 : 12-diphenylnaphthacene-5 : 11-dicarboxylic acid yields 1 : 2 : 4 : 5 : 6 : 7 : 9 : 10-*tetrabenzopyrene*-3 : 8-*quinone* [*ixone*] (**I**), dimorphous, m.p. 393—394°, reduced by $Na_2S_2O_4$ to the quinol (*diacetate*, m.p. 256—257°). (**I**) dyes (vat) cotton and rayon bright green.
W. C. J. R.

IV.—STEROLS AND STEROID SAPOGENINS.

Provitamin-*D*.—See B., 1942, III, 203.

Light absorption of geometrical isomerides and structure of vitamin-*D*.—See A., 1942, II, 280.

Photo-oxidation of cholesterol. A. Windaus, K. Bursian, and U. Riemann (*Z. physiol. Chem.*, 1941, **271**, 177—182).—Cholesterol, in a thin layer on a glass plate, was irradiated by ultra-violet light. Fractionation of the product by org. solvents and chromatograms afforded a hydroxycholesterol, m.p. 177° (*dibenzoate*, m.p. 133°; *bisdinitrobenzoate*, m.p. 176°), α-7-hydroxycholesterol, and Δ^4-*cholestene*-3 : 6-*diol*, m.p. >247° (diacetate, m.p. 133°; dibenzoate, m.p. 180—181°).
F. O. H.

Sterol fraction of Australian marine mollusca.—See A., 1942, III, 695.

Thiosteroids.—See B., 1942, III, 204.

3-Halogenobisnor*allo*cholanic acid compounds.—See B., 1942, III, 203.

Sterols. CXLII. 17-Methylpregnan-3(β)-ol-20-one and related compounds. R. E. Marker and R. B. Wagner (*J. Amer. Chem. Soc.*, 1942, **64**, 1273—1275).—Me 3(β)-acetoxy-17-methylætiocholanate (A., 1942, II, 230) and MgMeI in Et_2O, later boiling C_6H_6, give, by dehydration of the intermediate carbinol, 17-*methyl*-20-*methylene*-*pregnan*-3(β)-*ol*, m.p. 167—168° [*acetate* (**I**), m.p. 136—138°, stable to $POCl_3$–C_5H_5N at 135°], reduced by H_2–PtO_2 in AcOH at 3 atm. to 17 : 20-*dimethylpregnan*-3(β)-*ol*, m.p. 176—177°, and converted by O_3 in $CHCl_3$ into 17-*methylpregnan*-3(β)-*ol*-20-*one* (**II**), *forms*, m.p. 169—171° and 184—187°, also obtained from (**I**) by CrO_3–AcOH and subsequently 5% KOH–MeOH. CrO_3–AcOH oxidises (**II**) to 17-*methylpregnane*-3 : 20-*dione*, m.p. 131—134°. 3(β)-Acetoxy-17-methylætiocholanic acid by treatment with, successively, $SOCl_2$ at 0—5°, CH_2N_2–Et_2O, and gaseous HCl–Et_2O gives 17-*methylpregnane*-3(β) : 21-*diol*-20-*one*, m.p. 140—142°, but the chloride acetate with $ZnMe_2$ in tetrahydronaphthalene–N_2 at room temp. and later 100° and then 5% KOH–MeOH gives (**II**).
R. S. C.

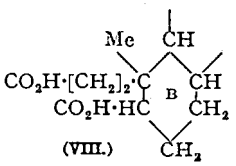
Sterols. CXLIII. Conversion of Δ^5-pregnen-3(β)-ol-20-one into dehydro*iso*androsterone. R. E. Marker, H. M. Crooks, jun., E. M. Jones, and A. C. Shabica (*J. Amer. Chem. Soc.*, 1942, **64**, 1276—1280).—3(β)-Acetoxy-Δ^5-pregnen-20-one (**I**). and MgMeI in Et_2O (later boiling C_6H_6) give 20-*methyl*-Δ^5-*pregnene*-3 : 20-*diol*, m.p. 194—195°, converted by boiling AcOH and later Ac_2O into 3(β)-*acetoxy*-20-*methyl*-$\Delta^{5:17}$-*pregnadiene*, m.p. 139—141° [corresponding 3(β)-*OH*-compound, m.p. 72°; some migration of the ethylenic linking into the ring is indicated by isolation of acid after ozonolysis of (**II**) (below)]. With Br (1 mol.) in $CHCl_3$ at −5°, this gives the 5 : 6-dibromide (**II**), converted by O_3 and then Zn dust–AcOH into dehydro*iso*androsterone acetate (**III**). 20-*Methylpregnane*-3(β) : 20-*diol*, m.p. 170—172°, obtained from pregnan-3(β)-ol-20-one by MgMeI, gives by dehydration ? 3(β)-*acetoxy*-20-*methylenepregnane*, m.p. 133—135°, and thence by ozonolysis and hydrolysis ætiocholan-3(β)-ol-20-one. (**I**) or 3(β)-*propionoxy*-Δ^5-*pregnen*-20-*one*, m.p. 119—120°, with Br (3 mols.) in AcOH gives 5 : 6 : 17 : 21-*tetrabromo*-3(β)-*acetoxy*- (**IV**), m.p. 172° (decomp.), or in $EtCO_2H$ gives -3(β)-*propionoxy*-*pregnan*-20-*one*, m.p. 175° (decomp.) (also obtained from the OH-compound in AcOH or PrOH, respectively). With Fe–AcOH at 100°, (**IV**) regenerates (**I**), and with NaI in boiling EtOH and then KOH–MeOH gives 3(β)-*hydroxy*-$\Delta^{5:17}$-*pregnadiene*-21-*carboxylic acid* (**V**), m.p. 252—253° (digitonide), which is hydrogenated (PtO_2; AcOH; 3 atm.) to allo*pregnan*-3(β)-*ol*-21-*carboxylic acid*, m.p. 228—230° [acetate, m.p. 191—193°, affords as above (Br, O_3, Zn–AcOH) (**III**)]. Reichstein's supposed (**V**) (A., 1939, II, 318; m.p. 217—218°) may have been the $\Delta^{5:16}$-isomeride.
R. S. C.

Sterols. CXLIV. 16-Alkyl-pregnenolones and -progesterones. R. E. Marker and H. M. Crooks, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 1280—1281).—$\Delta^{5:16}$-Pregnadien-3(β)-ol-20-one or its acetate with an excess of MgRHal in Et_2O, later boiling PhMe, gives (cf. Whitmore *et al.*, A., 1941, II, 170) 16-*methyl*- (**I**) (~30%), +*x*$COMe_2$, m.p. 191—192° [*semicarbazone*, m.p. 245° (decomp.); *acetate*, m.p. 177·5—178·5°], 16-iso*propyl*- (**II**), m.p. 157—158° (*acetate*, m.p. 131—132°; no semicarbazone), and 16-tert.-*butyl*-Δ^5-*pregnen*-3(β)-*ol*-20-*one* (**III**), m.p. 189—192° (*acetate*, m.p. 156—158°; no semicarbazone), oxidised by $Al(OBu^t)_3$–$COMe_2$–PhMe to 16-*methyl*-, m.p. 133—135°, 16-iso*propyl*-, m.p. 106·5—108°, and 16-tert.-*butyl*-*progesterone*, m.p. 154—155°, respectively. (**I**) is accompanied by (?) $\Delta^{5:16}$-bisnorcholadiene-3(β) : 20-diol (~35%) (*acetate*, m.p. 173—175°). With Na–EtOH, (**II**) gives a difficultly crystallisable substance, m.p. 130—134°, and (**III**) gives a *compound*, $C_{25}H_{42}O_2$, m.p. 178—180°.
R. S. C.

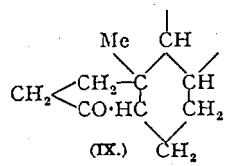
Sterols. CXLV. 21-Benzylidene-Δ^5-pregnen-3(β)-ol-20-one and allied compounds. R. E. Marker, E. L. Wittle, E. M. Jones, and H. M. Crooks, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 1282—1283).—3(β)-Acetoxy-21-benzylidenepregnan-20-one (A., 1939 II, 371) with CrO_3–AcOH at 60—90° and later KOH–EtOH gives 3(β)-*hydroxy*-*ætiocholanic acid* (70%), m.p. 229—230° (*Me* ester, m.p. 138—142°; *acetate*, m.p. 188—190°). 3(α)-*Hydroxyætio*allo*cholanic acid*, m.p. 282—285° (*acetate*, m.p. 208—210°), is similarly prepared from *epiallo*pregnanolone by way of the non-cryst. CHPh derivative. 21-*Benzylidene*-Δ^5-*pregnen*-3(β)-*ol*-20-*one* (**I**) (prep. from the OAc-ketone by PhCHO–NaOEt–EtOH at room temp.), m.p. 130—131° (gas), gives an *acetate* (**II**), m.p. 180—182°, which with, successively, Br–$CHCl_3$ at <0°, CrO_3 in 80% AcOH at 50°, Zn–AcOH at 100°, and boiling 2% KOH–MeOH gives 3(β)-*hydroxy*-Δ^5-*ætiocholenic acid*, m.p. 273—274°. With $Al(OBu^t)_3$–$COMe_2$–PhMe, (**I**) gives 21-*benzylidene*-*progesterone*, m.p. 155—158°. Hydrogenation (3% Pd–$BaSO_4$; dioxan; 3 atm.) of (**II**) gives 3(β)-*acetoxy*-21-*benzyl*-Δ^5-*pregnen*-20-*one*, *forms*, m.p. 128—129° and 143—145°, hydrolysed by $KHCO_3$ in boiling 70% MeOH to the *OH*-compound, m.p. 135—136°, which, as above, affords 21-*benzylprogesterone*, m.p. 86—88°.
R. S. C.

Toad poisons. XI. Constitution of bufotalin [etc.]. H. Wieland and H. Behringer (*Annalen*, 1941, **549**, 209—237; cf. A., 1937, II, 208).—Location of the *tert.* OH and OAc of bufotalin (**I**) at $C_{(14)}$ and $C_{(5)}$, respectively, is confirmed. Substances of the series are

renamed as derived from a saturated, OH-free lactone termed bufotalane. Male and female *Bufo vulgaris* yield, per animal, respectively, moist 31 and 64, and dry secretion 16·1 and 27·3 mg., including pure bufotalin 0·55 and 1·23 mg.; each yields crude bufotoxin 1·34, pure bufotenin 0·05, and bufotenidin 0·07 mg. per animal. Bufotaliene (**II**) (prep.: A., 1913, i, 1343; ~63%), $[\alpha]_D^{28}$ +404·6° in $CHCl_3$ (acetate, $[\alpha]_D^{29}$ +366·3° in $CHCl_3$), is accompanied by 3 : 14-*dihydroxybufotalatriene* (**III**) (~5—6%), +0·5EtOH, m.p. 182—183°, $[\alpha]_D^{28}$ +79·1° in $CHCl_3$ (*acetate*), stable to cold, conc. HCl [as also is (**II**)] but resinified by HCl–MeOH at 120°. H_2–Pd-black converts (**III**) in EtOH into non-cryst. acids and 3 : 14-*dihydroxybufotalane*, m.p. 138—140°. Hydrogenation (>5 H_2; Pd-black; EtOH) of (**II**) gives acids (20%), including hydroxy*iso*bufocholanic (**IV**), m.p. 153—154°, and a *hydroxycholenic acid*, m.p. 192—193° [with H_2–PtO_2 in AcOH gives (**IV**)], and α- (**V**) (64%), m.p. 204—205° (lit. 198—199°), $[\alpha]_D^{24}$ +56·0° in $CHCl_3$, and β-*hydroxybufotalane* (**VI**) (16%), m.p. 173·5—174·5°, $[\alpha]_D^{23}$ +30·8° in $CHCl_3$ (*acetate*, m.p. 153—154°). B_2O_3 at 270—275°/vac. dehydrates (**V**) and (**VI**) to α- (**VII**) (63%), m.p. 158—160°, and β-*bufotalene*, m.p. 136—138°, respectively, hydrogenated (Pd-black; EtOH) to α-, m.p. 153·5—155·5°, $[\alpha]_D^{19}$ +55·8° in $CHCl_3$ (with 0·1N-KOH–MeOH and then CH_2N_2 gives Me 21-hydroxybufocholanate, m.p. 82—83°), and β-*bufotalane*, m.p. 131—133°, $[\alpha]_D^{19}$ +37·4° in $CHCl_3$, respectively, probably epimerides at $C_{(20)}$. OsO_4 in AcOH converts (**V**) and (**VI**) into α- (50—60%), +EtOH, sinters at 100°, m.p. 104—108° (turbid; gas at 120°), and solvent-free, m.p. 156°, and β-*bufotalene glycol*, m.p. (+solvent) 93—100° (turbid; sinters at 90°; gas at 118°) or (solvent-free) 196—198° (sinters at 190°), oxidised by $Pb(OAc)_4$–AcOH to the α-, m.p. 251—253°, and β-*lactonedicarboxylic acid*, $C_{24}H_{36}O_6$ (**VIII**), m.p. 266—267°, respectively, which at 290° (N_2)

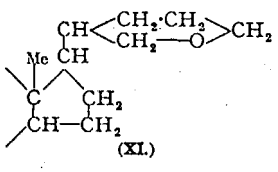


(VIII.)



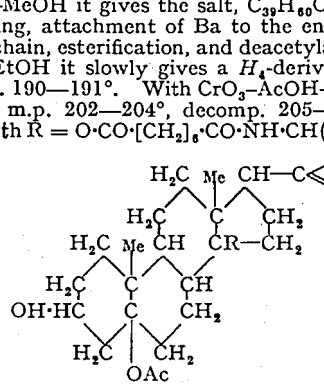
(IX.)

yield *ketones* (**IX**), $C_{23}H_{34}O_3$, m.p. 136—141° after sintering, and 177—183° (clear at 185°) after sintering, respectively. Hydrogenation (Pd-black; EtOH) of (**I**) gives α-, $[\alpha]_D^{18}$ +28·4° in $CHCl_3$, and β-*tetrahydrobufotalin*, sinters at 193°, m.p. 194—195°, $[\alpha]_D^{18}$ +35·7° in $CHCl_3$, converted by KOH–MeOH at room temp. into α-, +EtOH, foams at 149°, m.p. 217—218°, and β-3 : 5 : 14 : 21-*tetrahydrobufocholanic acid*, m.p. 188—189°, which at 150—160°/high vac. are lactonised to yield α- (**X**), m.p. 208—210°, and β-3 : 5 : 14-*trihydroxybufotalane*, respectively. CrO_3 oxidises (**X**) to 3 : 14-*dihydroxybufotalan*-3-*one*, m.p. 222—223°. H_2–PtO_2–AcOH reduces (**V**) or (**VII**) to *deoxobufotalane* (**XI**) (70%), $C_{24}H_{40}O$, m.p. 182—183° (no active H), which is also obtained from α-bufotalanone (**XII**) by Zn–Hg–HCl–EtOH and with P–HI (*d* 1·7) at 150—160° gives a *substance*, $C_{24}H_{41}OI$, b.p. 265—268°/0·001 mm. Hydrogenation (1 H_2) of (**XII**) in AcOH + HBr (little) gives a 3-*hydroxybufotalane*, m.p. 176—178°, but H_2–PtO_2 in EtOH–Et_2O (1 : 1) gives (**V**). H_2–PtO_2 in AcOH converts (**V**) into 3-*hydroxydeoxobufotalane* [as (**XI**)], m.p. 168·5—170·5° (1 active H).



(XI.)

Bufotoxin, $[\alpha]_D^{24}$ +3·9°, $[\alpha]_D^{19}$ +3·6° in MeOH, separates as $C_{40}H_{60}O_{10}N_4$, +EtOH; when dried and kept in air, it gives a *monohydrate*. It neutralises 0·22 equiv. of NaOH in 70% EtOH at once and 2·22—2·23 NaOH after 2 days and contains 1 OAc. With 0·1N-$Ba(OH)_2$–MeOH it gives the salt, $C_{39}H_{60}O_{10}N_4Ba$, by opening of the lactone ring, attachment of Ba to the enolic OH and the CO_2H of the side-chain, esterification, and deacetylation. With H_2–Pd-black in 70% EtOH it slowly gives a H_4-derivative, +EtOH, sinters at 180°, m.p. 190—191°. With CrO_3–AcOH–H_2O it gives *bufotoxinone*, +EtOH, m.p. 202—204°, decomp. 205—206°. Its formula is as shown, with R = O·CO·$[CH_2]_6$·CO·NH·CH(CO_2H)·$[CH_2]_3$·N:C(NH_2)$_2$.



[With G. Hesse and K. Gäbelein.] Skins of *Bufo arenarum* yield bases (bufotenine and bufothionine), *arenobufogenin*, $C_{24}H_{32}O_6$ (1 mg. per skin), m.p. 252° (decomp.) (cf. Jensen *et al.*, A., 1930, 1205; 1933, 1197; 1935, 1502) (feeble Liebermann reaction; reduces Tollens' reagent immediately), and *arenobufotoxin* (**XIII**), $C_{24}H_{30}O_5$·$C_{14}H_{24}O_4N$ (2 mg. per skin), decomp. (+3H_2O) 204° or (anhyd.) 214°. (**XIII**) gives a positive Liebermann and strong Sakaguchi reaction, contains no Ac, neutralises 0·52 NaOH in MeOH at once and 2·1 NaOH during 2 days, and is hydrolysed by boiling 0·5N-HCl–EtOH to CO_2H·$[CH_2]_6$·CO_2H and a *substance*, (?) $C_{24}H_{26}O_3$, m.p. 195°. R. S. C.

Lactone ring of scilliroside.—See A., 1942, II, 279.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Oxidation of trans-Δ²-menthene. W. Hückel and K. Kümmerle (*J. pr. Chem.*, 1942, [ii], **160**, 74—82; cf. A., 1940, II, 227).—*trans*-Δ²-Menthene and $Pb(OAc)_4$–AcOH at 85—90° (cf. Criegee, A., 1930, 1278) afford menthenol acetate, menthanediol diacetate, and a small amount of triacetate (monoacetate monoacetylglycollate of menthanediol), hydrolysed by aq. NaOH–MeOH to *p*-menthen-1-ol [hydrogenated (Pd–$BaSO_4$–EtOH) to *p*-menthan-1-ol], *p*-menthane-2 : 3-diol (**I**) [*diphenylurethane*, m.p. 149—151°; cf. isomeride, m.p. 83—85°, obtained from menthane-2 : 3-diol (**II**) prepared from menthene oxide (*loc. cit.*)], and K glycollate, respectively. (**I**) or (**II**) is further oxidised by $Pb(OAc)_4$–AcOH to α-methyl-α′-*iso*propyladipdialdehyde (di-2 : 4-dinitrophenylhydrazone, m.p. 155—156°). Oxidation of (**II**) by $KMnO_4$ gives a lactonic acid (**III**) (*loc. cit.*) and a non-cryst. mixture which is methylated (CH_2N_2) to 90% of the Me_2 ester of α-methyl-α′-*iso*propyladipic acid, b.p. 90—92°/0·85 mm., + 10% of the ester derived from (**III**). A. T. P.

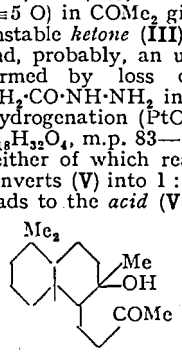
Terpinyl ethers.—See B., 1942, II, 281.

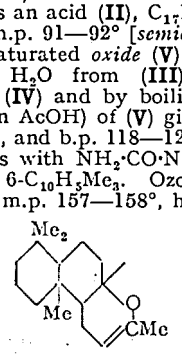
Oxidation of β-pinene by selenium dioxide. L. M. Joshel and S. Palkin (*J. Amer. Chem. Soc.*, 1942, **64**, 1008—1009).—β-Pinene and SeO_2 (0·4 mol.) in abs. EtOH give pinocarveol (29% pure) and a little (?) impure carvopinone (cf. lit.). R. S. C.

Oxidative cleavage of cyclic α-keto-alcohols by lead tetra-acetate. II. E. Baer (*J. Amer. Chem. Soc.*, 1942, **64**, 1416—1421; cf. A., 1940, II, 297).—*cyclo*Hexan-1-ol-2-one and $Pb(OAc)_4$ in AcOH containing a little H_2O yield CO_2H·$[CH_2]_4$·CHO, b.p. 144°/8 mm. (*trimeride*, m.p. 130·5—131°, formed on keeping; 2 : 4-*dinitrophenylhydrazone*, m.p. 140—141°) (cf. Treibs, A., 1939, II, 376; Harries *et al.*, A., 1908, i, 967); in AcOH–EtOH δ-*carbethoxy*-n-*valeraldehyde* (74·5%), b.p. 97—98°/10 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 74—75°), results. 2-Hydroxy*epi*camphor and $Pb(OAc)_4$ in AcOH+H_2O yield *camphoric acid* tert.-*semialdehyde* (**I**), m.p. 76—77·5° (76—78°), $[\alpha]_D$ +112·2° (+109·5°) in C_6H_6 (cf. Brcdt, A., 1917, i, 560), and in AcOH + EtOH give the *Et* ester (45·7%), b.p. 78—83°/0·2—0·3 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 183—184·5°; *semicarbazone*, m.p. 162·5—163·5°, $[\alpha]_D$ +44·9° in dry EtOH; with NaOH–EtOH gives (**I**)], of (**I**). (**I**) is indifferent to NaOI, $AgNO_3$–aq. NH_3, or dimedone, but its structure is proved by formation of a Me ester (by HCl–MeOH), b.p. 130—132°/8 mm., $[\alpha]_D^{25}$ +52·2° (homogeneous), $[\alpha]_D$ +51·4° in dry EtOH, 2 : 4-*dinitrophenylhydrazone*, m.p. 220—220·5°, semicarbazone, m.p. 204·5—206°, $[\alpha]_D$ +59·5° in EtOH, and oxime, m.p. 160—161°, $[\alpha]_D$ +62·2° in dry MeOH, neutralisation by 1 NaOH, and oxidation by HNO_3 at 100° to camphoric acid (89·3%). 3-Hydroxycamphor and $Pb(OAc)_4$ in AcOH + H_2O give *camphoric acid* sec.-*semialdehyde* (**II**) (95·2%), m.p. 126—127·5°, $[\alpha]_D$ +36·6° to +38·0° in C_6H_6 (2 : 4-*dinitrophenylhydrazone*, m.p. 223·5—224°; *oxime*, m.p. 142—143·5°, $[\alpha]_D$ −8·6° in dry MeOH; *semicarbazone*, m.p. 199—199·5°, $[\alpha]_D$ +11·9° in dry MeOH), or in AcOH + EtOH give the *Et* ester (48%), b.p. 88·5—89·5°/0·55 mm., $[\alpha]_D^{20}$ +21·2° in dry C_6H_6 (2 : 4-*dinitrophenylhydrazone*, m.p. 175—176°; reduces $AgNO_3$–aq. NH_3). R. S. C.

Dependence of optical rotatory power on chemical constitution. XIX. Stereoisomeric aminoanilino- and dimethylaminoanilinomethylenecamphors and their derivatives. B. K. Singh and B. Bhaduri (*Proc. Indian Acad. Sci.*, 1942, **15, A**, 281—292).—The following are prepared by condensing the requisite base with hydroxymethylenecamphor (**I**) in glacial AcOH: m-*acetamidoanilino*-d-, m.p. 211—213°, -l-, m.p. 211—213°, and -dl-, m.p. 216—218°, -*methylenecamphor*; m-*aminoanilino*-d-, m.p. 64—65°, -l-, m.p. 64—65°, and -dl-, m.p. 64—65°, -*methylenecamphor*; p-*aminoanilino*-d- (**II**), m.p. 163—164°, -l-, m.p. 163—164°, and -dl-, m.p. 163—164°, -*methylenecamphor*; meso-p-*phenylenediaminomethylenecamphor*, m.p. 269—270°; p-*dimethylaminoanilino*-d-, m.p. 169—170°, -l-, m.p. 169—170°, and -dl-, m.p. 169—170°, -*methylenecamphor*. (**II**) and *d*-camphorquinone at 100° in presence of fused Na_2SO_4 afford *anilinomethylene*-d-*camphor*-4-*imino*-d-*camphor*, m.p. 269—270°. [α] is recorded for many λλ and solvents. The rotatory power of these compounds obeys the simple Drude law. For such compounds comparison of the vals. of abs. sp. rotation may be made; these are equal numerically to *k* of Drude's equation when $\lambda = \sqrt{(\lambda_0^2 + 1)}$ (always in the infra-red region). The influence of different groups in order of their decreasing rotatory power is $NH_2 > NMe_2 > H > Me > Cl > Br > I$, which agrees well, subject to minor variations, with the polar series as well as with the sequence of the dissociation consts. of the substituted anilines with which (**I**) is condensed. H. W.

Diterpenes. LIII. Oxidation of sclareol with potassium permanganate. L. Ruzicka, C. F. Seidel, and L. L. Engel (*Helv. Chim. Acta*, 1942, **25**, 621—630).—Oxidation of sclareol (**I**) with $KMnO_4$ (≡5 O) in $COMe_2$ gives an acid (**II**), $C_{17}H_{34}O_4$, m.p. 153—154°, an unstable *ketone* (**III**), m.p. 91—92° [*semicarbazone* (**IV**), m.p. 145°], and, probably, an unsaturated *oxide* (**V**), m.p. 174—176°/10 mm., formed by loss of H_2O from (**III**). (**V**) is converted by $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ into (**IV**) and by boiling aq. EtOH into (**III**). Hydrogenation (PtO_2 in AcOH) of (**V**) gives a mixture of *products*, $C_{18}H_{32}O_4$, m.p. 83—84°, and b.p. 118—120°/0·25 mm., respectively, neither of which reacts with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$. Se at 340—350° converts (**V**) into 1 : 5 : 6-$C_{10}H_5Me_3$. Ozonisation of (**V**) in *n*-C_6H_{14} leads to the *acid* (**VI**), m.p. 157—158°, hydrolysed to the (impure)


(III.)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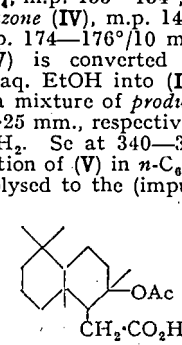
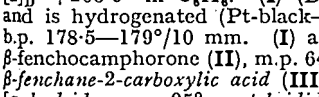
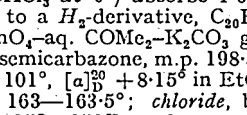

(VI.)

OH-acid, m.p. 128—129°, which passes by loss of H_2O into the lactone (**VII**), $C_{16}H_{26}O_2$, m.p. 123—124°, $[\alpha]_D$ +45·9° in $CHCl_3$, obtained previously by oxidation of (**I**) with CrO_3. (**VII**) is converted by HBr in boiling EtOH into an isomeric *lactone*, m.p. 133—134°, $[\alpha]_D$ −55·3° in $CHCl_3$, which does not contain OAlk. Energetic oxidation of (**II**) with $KMnO_4$ yields (**VII**). (**II**) gives a *Me* ester, m.p. 111—112°. (**III**) is transformed by $Mg(ClO_4)_2$ in boiling PhMe into the unsaturated *ketone*, b.p. 130—135°/0·4 mm. (*semicarbazone*, $C_{19}H_{33}ON_3$, m.p. 197—198°). H. W.

Chemistry of synthetic diterpenes. I. Dimerisation of fenchene with clay catalysts: β-difenchene. N. J. Toivonen, V. Alfthan, L. H. Böök, M. I. Erich, and E. K. Heino (*J. pr. Chem.*, 1941, [ii], **159**, 70—114).—*d*-β-Difenchene (**I**), m.p. 83°, b.p. 171°/10 mm., $[\alpha]_D^{20}$ +67·7° in C_6H_6 [HCl–AcOH at −5° gives the *hydrochloride*, m.p. 79°, $[\alpha]_{D\ c}^{21\cdot5}$ −35·7° in C_6H_6, from which (**I**) is regenerated by boiling KOH–EtOH or in quinoline at 150°; the *hydrobromide*, m.p. 76—78°, $[\alpha]_D^{20}$ −66·1° in C_6H_6, gives (**I**) with KOH–EtOH at room temp. or by air at 70°], is one of the products obtained from *cyclo*fenchene in presence of Florida earth, with or without C_6H_6 or ligroin (cf. A., 1936, 1259). A mixture of *cyclo*- and α-fenchene similarly yields polymerides and *l*-β-difenchene, m.p. 83°, $[\alpha]_D^{22\cdot2}$ −66·3° in $CHCl_3$ (*hydrochloride*, m.p. 79°, $[\alpha]_D^{21\cdot5}$ +35·7° in C_6H_6). *dl*-β-Difenchene affords a hydrochloride, m.p. 80°. (**I**) and Br in AcOH give a *Br*-derivative, $C_{20}H_{31}Br$, m.p. 48—49°, $[\alpha]_D^{20\cdot5}$ +304·6° in C_6H_6, or in $CHCl_3$ a Br_2-compound, $C_{20}H_{30}Br_2$, m.p. 108—109·5°, $[\alpha]_D^{21}$ +203·9° in C_6H_6. (**I**) (BzO_2H–$CHCl_3$ at 0°) absorbs 1·6 O, and is hydrogenated (Pt-black–AcOH) to a H_2-derivative, $C_{20}H_{34}$, b.p. 178·5—179°/10 mm. (**I**) and $KMnO_4$–aq. $COMe_2$–K_2CO_3 give β-fenchocamphorone (**II**), m.p. 64—65° (semicarbazone, m.p. 198·5°), *β-fenchane-2-carboxylic acid* (**III**), m.p. 101°, $[\alpha]_D^{20}$ +8·15° in EtOH [*anhydride*, m.p. 95°; *o-toluidide*, m.p. 163—163·5°; *chloride*, b.p. 106—106·5°/10 mm.; *amide* (**IV**), m.p. 172—173°], and a neutral


(I.)


(VI.)

product, $C_{20}H_{32\ or\ 34}O_2$, m.p. 201—202°, probably dihydroxydihydro-β-difenchene, which is decomposed by distillation at 300° or by CrO_3–AcOH at 50° to an aldehyde, $C_{11}H_{18}O$ (*semicarbazone*, m.p. 182—185°), probably corresponding with (**III**). (**I**) and O_3 yield (**II**), (**III**), a (δ-)*lactone*, m.p. 118·5°, of 4 : 4-dimethyl-3-hydroxymethyl-*cyclo*pentanecarboxylic acid or of 3-hydroxy-5 : 5-dimethyl*cyclo*pentylacetic acid [also obtained from (**II**) and Caro's acid], and β-fenchene hydrate (**V**), m.p. 67—68° (phenylurethane, m.p. 92—93°), also obtained from *iso*fenchyl chloride and aq. KOH (cf. *r*-form; Komppa *et al.*, A., 1933, 830). (**IV**) and aq. NaOBr–NaOH–Br at 0° yield *β-fenchanecarbamide* (**VI**), m.p. 285°, $[\alpha]_D^{27}$ +27·3° in $CHCl_3$, converted by distillation with KOH into 2-*amino-β-fenchane* (**VII**) (Bz_2 derivative, m.p. 159·5—160°). Distillation of the corresponding *hydrochloride*, m.p. 242—244° (decomp.) (anhyd.), or $+H_2O$, m.p. 74°, $[\alpha]_D^{24}$ +8·69° in EtOH, affords β- + γ-fenchene (*d*-fenchone series), as also does (**V**), obtained from the hydrochloride and aq. KNO_2. β-Fenchene is hydrogenated (Pt-black–MeOH) to β-fenchane, nitrated (HNO_3, *d* 1·075, at 130—135°) to the NO_2-compound, m.p. 111°, $[\alpha]_D^{16}$ +5·46° in EtOH, convertible by distillation into (**II**) or by reduction (Sn–HCl–EtOH) into (**VII**). α-Fenchane affords a NO_2-compound, m.p. 57—58°, $[\alpha]_D^{22}$ −84·1° in EtOH, converted by distillation into α-fenchocamphorone (*semicarbazone*, m.p. 220—221°) or by reduction into 2-*amino-α-fenchane*, m.p. 26—27·5°, b.p. 201·3—201·5°/765 mm. [*hydrochloride* (**VIII**), decomp. 270°, $[\alpha]_D^{26\cdot5}$ −25·9° in EtOH; *Bz* derivative, m.p. 155—155·5°]. Dry distillation of (**VIII**) affords terpenes, b.p. 148·5—153·5° and 153·5—157·5°/752 mm., oxidised to impure α-hydroxyfenchenecarboxylic acid (derived from α-fenchene, with no γ-compound). Isomerisation of (**I**) occurs in presence of Florida earth, and this isomeride is probably one of the by-products obtained during prep. of (**I**). A. T. P.

History of the chemistry of the terpenes. W. Hückel (*Naturwiss.*, 1942, **30**, 17—30). H. W.

Synthesis of 5-methylazulene.—See A., 1942, II, 280.

VI.—HETEROCYCLIC.

Reaction products from α-chloroketones and potassium cyanide. II. Action of potassium cyanide on chloroacetone; so-called "dimeric cyanoacetone." R. Justoni (*Gazzetta*, 1941, **71**, 41—53; cf. A., 1939, II, 406).—The product from KCN and $CH_2Cl{\cdot}COMe$ (**I**) is not "dimeric cyanoacetone," $COMe{\cdot}CH(CN){\cdot}CMe(OH){\cdot}CH_2{\cdot}CN$ (cf. Obregia, A., 1892, 324), but 5-*hydroxy*-2 : 4-*dicyano*-2 : 5-*dimethyltetrahydrofuran* (**II**), m.p. 183° [formed by cyclisation of the intermediate $COMe{\cdot}CH(CN){\cdot}CH_2{\cdot}CMe(OH){\cdot}CN$], also obtained from $CH_2Cl{\cdot}CMe(OH){\cdot}CN$ [new prep. from (**I**) and anhyd. HCN] and aq. $COMe{\cdot}CHNa{\cdot}CN$ (**III**), or by interaction of (**I**) and (**III**) in MeOH to give the *Na* derivative of *cyanoacetonylacetone*, b.p. 106—108°/3 mm. [*bis*-p-*nitrophenylhydrazone* (**IV**), m.p. 227°], which with aq. KCN and HCl gives (**II**). In boiling H_2O, (**II**) evolves HCN. In dil. NaOH, (**II**) with *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ in AcOH gives (**IV**). The product from (**II**) and dil. H_2SO_4 is not the δ-lactone of $OH{\cdot}CMe{:}C(CN){\cdot}CMe(OH){\cdot}CH_2{\cdot}CO_2H$ (cf. Obregia, *loc. cit.*), but *γ-hydroxy-γ-cyano-α-acetylvaleric acid γ-lactone* (p-*nitrophenylhydrazone*, m.p. 151—152°), which is hydrolysed to $(CH_2{\cdot}COMe)_2$. E. W. W.

Furancarboxylic acid derivatives.—See B., 1942, II, 315.

Complex kojates of transition elements.—See A., 1942, I, 291.

Chemistry of vitamin-*E*. XXXVIII. α-Tocopheramine, a new vitamin-*E* factor. XXXIX. Calcium α-tocopheryl succinate. L. I. Smith, W. B. Renfrow, jun., and J. W. Opie (*J. Amer. Chem. Soc.*, 1942, **64**, 1082—1084, 1084—1086; cf. A., 1942, II, 234).—XXXVIII. 1 : 2 : 3 : 5 : 4-$OH{\cdot}C_6HMe_3{\cdot}NH_2$,HCl in boiling HCO_2Na–HCO_2H gives the *CHO* derivative, m.p. 213—214°, which with anhyd. $CuSO_4$–phytol–N_2 at 135° gives *α-tocopheramine* [5-*amino*-4 : 6 : 7-*trimethyltocol*] (**I**), b.p. 285—288°/1—2 mm. (oxalate, m.p. 153—154°), isolated after chromatography (Al_2O_3) as *hydrochloride*, anhyd. and +0·5H_2O, m.p. 155—157°. The structure of (**I**) is proved by oxidation by $FeCl_3$–HCl–MeOH–H_2O to the quinone (**II**), reduction, and cyclisation to α-tocopherol (**III**). The vitamin-*E* activity of (**I**) equals that of (**III**) but is probably not due to biological oxidation to (**II**) since (**II**) is inactive.

XXXIX. The MgBr derivative (prep. by MgRBr) of 6-hydroxy-2 : 2 : 5 : 7 : 8-pentamethylchroman (not the chroman in alkali) with $ClCO_2Et$– or $CH_2Cl{\cdot}COCl$–Et_2O at room temp. gives the Et carbonate, m.p. 50—52°, and chloroacetate, m.p. 112—114°, respectively, and with $(CH_2{\cdot}CO)_2O$–Et_2O–dioxan at room temp. and later 100° gives the *H succinate*, m.p. 138—139·5°, rapidly hydrolysed by 2% NaOH at room temp. The MgBr derivative of (**III**) gives similarly the H succinate [*Ca* salt (**IV**), m.p. various, 194—198° to 225° (softens at 220°)]. The vitamin-*E* activity of (**IV**) equals that of (**III**). R. S. C.

Antisterility factors (vitamin-*E*). X. Synthesis of nor-α-tocopherol. W. John and H. Herrmann (*Z. physiol. Chem.*, 1942, **273**, 191—198).—α-5-Hydroxy-2-methoxy-3 : 4 : 6-trimethylphenylbutan-γ-one is converted by $BaCO_3$ and boiling AcCl into its *acetate* (**I**), m.p. 80°, which gives a non-cryst., ill-defined acetal with $CH_2Cl{\cdot}OMe$. (**I**) is converted by Mg hexahydrofarnesyl bromide followed by hydrolysis (KOH–MeOH) and oxidation ($FeCl_3$) of the product into the non-cryst. quinone, which with Zn dust and HBr (*d* 1·49) in AcOH gives *nor-α-tocopherol* (**II**), $OH{\cdot}C{:}CMe{\cdot}C(CH_2{\cdot}CH_2{\cdot}MeC{:}CMe{\cdot}C{\cdot}O{\cdot}CMe{\cdot}C_{15}H_{31})$, an oil (*allophanate*, m.p. 170—172°), which is biologically somewhat less active than α- and at least as active as natural β- or γ-tocopherol. (**II**) is oxidised to nor-α-tocopherylquinone, which is reductively esterified with *p*-$C_6H_4Br{\cdot}COCl$ to the *di*-p-*bromobenzoate* of *nor-α-tocopherylquinol*, m.p. 105°. (**I**) and MgMeI in Et_2O–C_6H_6 afford β-5-hydroxy-2-methoxy-3 : 4 : 6-trimethylphenylethyldimethylcarbinol, m.p. 105°. *iso*-α-Tocopherol, m.p. 65°, is obtained by a similar series of reactions from (**I**), Mg, and cetyl chloride; it is characterised as the *di*-p-*bromobenzoate* of iso-*α-tocopherylquinol*, m.p. 102°. H. W.

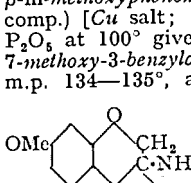
Pechmann condensation of phenols with ethyl γ-phenylacetoacetate. N. G. Kotwani, S. M. Sethna, and G. D. Advani (*J. Univ. Bombay*, 1942, **10**, **A**, *Part* 5, 143—146).—Et γ-phenylacetoacetate condenses with phenols in presence of H_2SO_4 giving 4-benzylcoumarins. *m*-$C_6H_4(OH)_2$ yields 7-hydroxy-4-benzylcoumarin, m.p. 214—215° (*acetate*, m.p. 138—139°; *benzoate*, m.p. 180—181°; *Me ether*, m.p. 140—141°), which affords (Me_2SO_4, NaOH then HCl) 2 : 4-*dimethoxy-β-benzylcinnamic acid*, m.p. 130°. Orcinol yields *5-hydroxy-4-benzyl-7-methylcoumarin*, m.p. 248—249° (*acetate*, m.p. 139—140°; *Me ether*, m.p. 140—141°), which affords 2 : 6-*dimethoxy-4-methyl-β-benzylcinnamic* acid, m.p. 153—154°. Pyrogallol yields 7 : 8-*dihydroxy-4-benzylcoumarin*, m.p. 192—194° (*diacetate*, m.p. 168°; *Me_2 ether*, m.p. 178—180°). Phloroglucinol yields 5 : 7-dihydroxy-4-benzylcoumarin, m.p. 274—276° [lit. 260° (decomp.)] (*diacetate*, m.p. 152—154°; *Me_2 ether*, m.p. 182—183°), which affords

2 : 4 : 6-*trimethoxy-β-benzylcinnamic acid*, m.p. 144—146°. α-$C_{10}H_7$·OH yields *4-benzyl-α-naphthacoumarin*, m.p. 174°. PhOH, β-$C_{10}H_7$·OH, quinol, *m*-cresol, Me β-resorcylate, and resacetophenone do not condense. It appears that the Ph has a considerable inhibiting effect. W. C. J. R.

Condensation of chalkones with flavanones. B. N. Kaplash, R. C. Shah, and T. S. Wheeler (*J. Indian Chem. Soc.*, 1942, **19**, 117—120; cf. A., 1940, II, 102).—Ph (I) or *p*-tolyl styryl ketone condenses with flavanone (II) in presence of aq. NaOH–EtOH to give 3-α-*phenyl-β-benzoylethyl-*, m.p. 149—151° (2 : 4-*dinitrophenylhydrazone*, m.p. 229—230°), or -β-p-*toluoylethyl-flavanone* (2 : 4-*dinitrophenylhydrazone*, m.p. 237—239°), respectively. Ph 4′-methoxystyryl ketone and (II)–EtOH–NaOEt afford 3-α-p-*anisyl-β-p-toluoylethyl-flavanone*, m.p. 92—94° (+0·5H_2O), but Na–Et_2O was necessary to obtain 3-α-*anisyl-β-p-toluoylethyl-*, m.p. 90—92°, 3-α-p-*tolyl-β-benzoylethyl-* (+0·5H_2O) (2 : 4-*dinitrophenylhydrazone*, m.p. 252—255°), and 3-α-p-*tolyl-β-p-toluoylethyl-flavanone* (+H_2O) (2 : 4-*dinitrophenylhydrazone*, m.p. 244—251°), respectively, from (II) and the respective styryl ketone. 3′ : 4′-Methylenedioxyflavanone and (I) in Na–Et_2O yield 3′ : 4′-*methylenedioxy*-3-α-*phenyl-β-benzoylethyl-flavanone*, m.p. 184—185° (2 : 4-*dinitrophenylhydrazone*, m.p. 228—230°). (II) could not be condensed with Ph, *p*-tolyl-, *o*-hydroxy- or -methoxy-phenyl 3′ : 4′-methylenedioxystyryl ketone, 5-nitro-2-hydroxy-4-methoxyphenyl styryl ketone, or 5-nitro-2-hydroxy-4-methoxyphenyl 4′-methoxy- or -methyl-styryl ketone. A. T. P.

Isolation of hibiscitrin from the flowers of *Hibiscus sabdariffa*: constitution of hibiscetin. P. S. Rao and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **15**, **A**, 148—153).—EtOH-extraction of the dried petals yields *hibiscitrin*, $C_{27}H_{30}O_{19},H_2O$, m.p. 238—240° (decomp.; sinters 225°), hydrolysed (7% H_2SO_4) to hibiscetin (I), oxidised (*p*-benzoquinone in C_5H_5N) to the *quinone*, m.p. ∢350°, reduced by aq. SO_2 to (I). The Ac derivative of (I) with Me_2SO_4 + NaOH yields *hibiscetin Me*$_7$ *ether* (+2H_2O), m.p. 194—196°, which with 50% alkali yields 3 : 4 : 5 : 1-$C_6H_2(OMe)_3$·CO_2H. It is concluded that (I) is 3 : 5 : 7 : 8 : 3′ : 4′ : 5′-heptahydroxyflavone. A. Lr.

Synthesis of μ-amino-2-methoxyehromindan. P. Pfeiffer and H. Simons (*J. pr. Chem.*, 1942, [ii], **160**, 83—94).—*m*-OMe·C_6H_4·O·CH_2·CN and CH_2Ph·MgCl–Et_2O at room temp. afford *CH_2Ph* m-*methoxyphenoxymethyl ketone*, m.p. 48—49° [*oxime*, m.p. 63—74° (mixture); *semicarbazone*, m.p. 143°], converted by aq. KCN–$(NH_4)_2CO_3$ at 100° (CO_2) into 5-*benzyl*-5-m-*methoxyphenoxymethylhydantoin*, m.p. 178·5°, and thence (25% aq. KOH) α-*amino-β*-m-*methoxyphenoxy-β-phenylisobutyric acid*, m.p. 195—200° (decomp.) [*Cu* salt; *Ac* derivative (I), m.p. 232°]. (I) and H_3PO_4–P_2O_5 at 100° give two isomeric cyclic ketones, viz., 3-*acetamido*-7-*methoxy*-3-*benzylchromanone* [-2 : 3-*dihydro*-1 : 4-*benzpyrone*] (II), m.p. 134—135°, and 2-*acetamido*-2-m-*methoxyphenoxymethylindan*-1-*one* (III), m.p. 156°. (II) is reduced by Na–Hg (PO_4''' buffer) to the two isomeric 3-*acetamido*-7-*methoxy*-3-*benzyl*-*chromanols* [-4-*hydroxy*-2 : 3-*dihydro*-1 : 4-*benzpyrans*] (IV), m.p. 204° and 159°, respectively, and (III) affords the isomeric -*indan*-1-*ols*, m.p. 205° and 108°, respectively. Ring-closure (H_3PO_4 at 90°) of (IV) yields μ-*acetamido*-2-*methoxychromindan* (V), m.p. 164°, and thence the base (*hydrochloride*, m.p. 215—217°). A. T. P.



(V.)

Cœroxan compounds.—See B., 1942, II, 281.

Synthesis of 2′-ketodihydro-1 : 2-*cyclo*pentenophenanthrene and derivatives of phenanthro[1, 2-*b*]furan.—See A., 1942, II, 318.

Behaviour of γ-diketones.—See A., 1942, II, 300.

Dioxan derivatives.—See B., 1942, II, 315.

Substituted acetylenes and their derivatives. XLIV. Catalytic addition reactions of acetylenic alcohols. G. F. Hennion and W. S. Murray (*J. Amer. Chem. Soc.*, 1942, **64**, 1220—1222; cf. A., 1940, II, 187).—In presence of BF_3–HgO at 45—55°, CH:C·CH_2·OH (prep. from CH_2O and CH:CNa in liquid NH_3; 10% yield), b.p. 54°/57 mm., CH:CHMe·OH (61% yield), b.p. 46°/50 mm., and CH:C·CHPh·OH (58% yield), b.p. 80°/4 mm., give, by addition of MeOH and ring-closure, 2 : 5-*dimethoxy*-2 : 5-*dimethyl-* (5%), m.p. 125°, -2 : 3 : 5 : 6-*tetramethyl-* (41%), m.p. 77°, and 3 : 6-*diphenyl*-2 : 5-*dimethyl-* (36%), m.p. 254—256°, -1 : 4-*dioxan*. CH:C·$[CH_2]_2$·OH (65% yield), b.p. 50°/28 mm., gives only CH_2:C(OMe)·$[CH_2]_2$·OH (47%), b.p. 45·5°/20 mm., and impure $(OMe)_2CMe·[CH_2]_2$·OH (10%), b.p. 54—56°/5 mm. 1-Acetylenyl*cyclo*hexanol (87% yield), m.p. 32°, b.p. 68°/11 mm., gives an intractable mixture. Addition of $(CH_2·OH)_2$ in presence of BF_3–HgO at 65° gives 2-*methyl*-2-α-*hydroxyethyl-* (67%), b.p. 69°/11 mm., -2-α-*hydroxyisopropyl-* (57%), b.p. 70°/12 mm., and -2-1′-*hydroxycyclohexyl-* (63%), m.p. 56°, -1 : 3-*dioxolan*. With AcOH–BF_3–HgO at 55—65° there are formed OAc·CH_2·COMe (30%), b.p. 65°/11 mm., OAc·CHMe·COMe (41%), b.p. 56°/10 mm., *phenylacetylcarbinol acetate* (50%), b.p. 65°/11 mm., and 1-*acetylcyclohexyl acetate* (35%), b.p. 109°/11 mm. A little conc. HCl in boiling EtOH hydrolyses all the products to the corresponding acyloins and MeOH or AcOH. R. S. C.

Nature [dehydration and stabilisation] of furfuryl alcohol. A. P. Dunlop and F. N. Peters, jun. (*Ind. Eng. Chem.*, 1942, **34**, 814—817).—When furfuryl alcohol (I) is boiled alone or with H_2O, heated at 150° or with H_2O and a trace of HCl at 80°, or kept with H_2O at room temp. (3 months), dehydration leads to some (?) 5-2′-*furfurylfurfuryl alcohol* (II), b.p. 131—133°/2·5 mm. (absorbs 4 Br; α-*naphthylurethane*, m.p. 107—108°; *benzoate*, m.p. 70—71°), 2-2′-*furfuryl*-5-5″-*hydroxymethyl*-2″-*furfurylfuran* (III), b.p. 199—202°/3 mm. (absorbs 6 Br), and resins. Small amounts of (II) or (III) render much (I) insol. in H_2O and the purity of (I) is best determined by its cloud point, *i.e.*, the temp. at which a mixture with an equal vol. of H_2O becomes cloudy when cooled. Dehydration is prevented by inorg. or org. bases: *e.g.*, in 10·5 hr. at 150° the amount of dehydration [33% for (I) alone] is 0·4 and 1·1% in presence of 0·1% (larger amounts are not advantageous) of NH_2Bu^{α} and piperidine, respectively. Such stabilisation is probably advantageous during hydrogenation of (I). Dehydration accounts for the poor yield of lævulic acid obtained from (I) by acidic cleavage. R. S. C.

Additive compounds of tetrahydrothiopyran [pentamethylene sulphide]. H. J. Worth and H. M. Haendler (*J. Amer. Chem. Soc.*, 1942, **64**, 1232—1233).—$[CH_2]_5S$ (*A*) (prep. from Cl·$[CH_2]_5$·Cl by Na_2S in boiling EtOH) gives additive *compounds*. (i) (*A*),X in which X = $HgBr_2$, m.p. 101—105°, CuCl (prep. from CuCl or $CuCl_2$), m.p. 154·5—160°, CuBr (prep. from CuBr or $CuBr_2$), m.p. 123—124°, CuI, m.p. 164—165° (decomp.), $AuCl_3$, m.p. 120—122° (decomp.), AuCl, m.p. 179—182° (decomp.), $AuBr_3$ (I), m.p. 140—145° (decomp.), and AuBr [prep. from (I) by an excess of (*A*) in boiling EtOH], m.p. 173—179° (decomp.), and (ii) 2(*A*),X in which X = $SnCl_4$, m.p. 149—151·5°, $SnBr_4$, m.p. 149·5—151°, PtI_2, m.p. 194·5—196° (decomp.), and $PdCl_2$, m.p. 146·5—148·5° (decomp.). R. S. C.

Thioindigos.—See B., 1942, II, 318.

Identification of organic compounds. VI. Preparation of *p*-nitrobenzylpyridinium salts of aromatic sulphonic acids. E. H. Huntress and G. L. Foote (*J. Amer. Chem. Soc.*, 1942, **64**, 1017—1020; cf. A., 1942, II, 136).—RSO_3Ag and *p*-NO_2·C_6H_4·CH_2Cl in dry C_5H_5N at 100° give C_5H_5N p-*nitrobenzyl-benzene-*, m.p. 168°, -o-*toluene-*, m.p. 170°, -4-o-, m.p. 158·5°, and -p-*xylene-*, m.p. 139·5°, *-naphthalene*-2-, m.p. 148·5°, *-anthraquinone*-2-, m.p. 187°, -p-*hydroxy-*, m.p. 162°, -p-*amino-*, m.p. 211°, and -p-*acetamido-benzene-*, m.p. 79·5°, -2-*amino*-m-*toluene-*, m.p. 200°, -2-*aminonaphthalene*-1-, m.p. 142°, and -6-, m.p. 218° (decomp.) and +H_2O (lost at 110°), -2-*acetamidonaphthalene*-6-, m.p. (anhyd.) 172° and (+xH_2O) ~115°, -1-*aminonaphthalene*-4-, m.p. 176°, -5-, m.p. 169°, and -8-, m.p. 138°, -1-*acetamidonaphthalene*-4-, m.p. 193°, -5-, m.p. 159·5°, and -8-, m.p. 85°, *-sulphonate*. (C_5H_5N)$_2$ (*di*-p-*nitrobenzyl*)*benzene*-1 : 3-*disulphonate*, m.p. 204°, is similarly prepared. No such compounds can be obtained from Na salts or from Ag salts in EtOH. Boiling aq. NaOH causes the reactions, 3*p*-NO_2·C_6H_4·CH_2·NC_5H_5}RSO_3 + 3NaOH → *p*-CHO·C_6H_4·NO:N·C_6H_4·CHO-*p* + *p*-NO_2·C_6H_4·CHO + 3C_5H_5N + 3H_2O + 3RSO_3Na; C_5H_5N benzylhydroxide is the probable intermediate, since when prepared by Ag_2O from the chloride it is similarly decomposed. R. S. C.

3 : 4-Substituted pyridines. I. Synthesis of 4-methyl-3-vinylpyridine. J. R. Stevens, R. H. Beutel, and E. Chamberlin (*J. Amer. Chem. Soc.*, 1942, **64**, 1093—1095).—OEt·$[CH_2]_2$·CHAc·CO_2Et, b.p. 115°/10 mm. (lit. 85—90°/10 mm.), CN·CH_2·CO·NH_2, and aq. NH_3 at room temp. give the *NH_4* salt (34·6%) of 2 : 6-dihydroxy-3-cyano-4-methyl-5-β-ethoxyethylpyridine. α-Aceto-γ-butyrolactone, CN·CH_2·CO_2Et, and 28% aq. NH_3 give the *NH_4* salt (52%), m.p. indefinite, of 2 : 6-dihydroxy-3-cyano-4-methyl-5-β-hydroxyethylpyridine, which with boiling conc. HCl at the b.p. gives 6-*hydroxy*-5-*cyano*-4-*methyl*-4′ : 5′-*dihydrofurano*-2′ : 3′-2 : 3-*pyridine*, m.p. indefinite, but with conc. HCl at 150° (sealed tube) gives 6-hydroxy-4-methyl-4′ : 5′-dihydrofurano-2′ : 3′-2 : 3-pyridine, OH-, m.p. 250°, and pyridone *form*, m.p. 177·5—179° (cf. Robinson *et al.*, A., 1934, 1373), differentiated by $FeCl_3$ and absorption spectra. With $POCl_3$ at 120° this gives a *compound*, $C_8H_9ONCl_2$, m.p. 132·8°, and at 180° gives 2 : 6-*dichloro*-4-*methyl*-3-β-*chloroethylpyridine* (57%), m.p. 68·9°, reduced (H_2–PdCl$_2$–C; HCl–MeOH–H_2O) to 4-*methyl*-3-β-*chloromethylpyridine hydrochloride* (86·5%), m.p. 170—171°, which with hot KOH–MeOH gives 4-methyl-3-vinylpyridine (*hydrochloride*, m.p. 164—166°). R. S. C.

Nitrogen compounds in petroleum distillates. XXIII. Structure of a $C_{16}H_{25}N$ base from Californian petroleum. W. Shive, S. M. Roberts, R. I. Mahan, and J. R. Bailey (*J. Amer. Chem. Soc.*, 1942, **64**, 909—912; cf. A., 1942, II, 31).—The base, $C_{16}H_{25}N$ (I), m.p. 24·5°, b.p. 279—281°/747 mm. (picrate, m.p. 164°), from Californian petroleum is shown by the following and earlier data to be 2-1′ : 1′ : 3′-*trimethylcyclohexyl*-4 : 6-*dimethylpyridine* and is thus related to the acids from the same source. H_2–Raney Ni at 250°/2000—6000 lb. converts (I) into 2-1′ : 1′ : 3′-*trimethylcyclohexyl*-4 : 6-*dimethylpiperidine*, stereoisomerides, m.p. 60·5° and liquid, converted by BzCl in dry C_5H_5N at 27—30° into the 1-*Bz* derivative (II), m.p. 120·5°, b.p. 208—212°/3 mm., which with PBr_3–Br at 140° gives, after distillation, $POBr_3$, PhCN, and 1 : 1 : 3-*trimethyl*-2-γ-

methyl-$\Delta^{\alpha\delta}$-*hexadienyl*cyclo*hexane* (**III**) (mixture), b.p. 109—115°/6 mm., 260—267°/746 mm. (absorbs 4 Br). With O_3 in CCl_4, (**III**) gives *trans*-2 : 2 : 6-trimethyl*cyclo*hexanecarboxylic acid (**IV**) (29%), m.p. 82—83°. O_3 converts (**II**) in CCl_4 into an oil, RCO·N:CMeR', which with NaOH–H_2O_2 (not in acid or neutral solution) gives trans-2 : 2 : 6-*trimethyl*cyclo*hexanecarboxylamide* (23%), m.p. 190—191° (isolated because so stable), unaffected by 20% NaOH at 140° or by acid, but converted by KOBr at 0°, later 70°, into the amine obtained from (**IV**) by HN_3. R. S. C.

Stearoxyalkylpyridinium salts.—See B., 1942, II, 333.

Narcotic potency of biurets containing piperidine. H. H. Anderson, C. H. Ch'eng, S. P'an, P. P. T. Sah, and C. Lu (*Science*, 1942, **95**, 255—256).—5-*Phenyl*-1-*diphenylyl*-, m.p. 134°, 1-*phenyl*-5 : 5-*pentamethylene*-, m.p. 183°, 1 : 1-5 : 5-*bispentamethylene*-, m.p. 198°, and 5 : 5-*pentamethylene-biuret*, m.p. 121°, have been prepared. (See also A., 1942, III, 710.) E. R. S.

Cyanine dyes of the pyridine series. II. M. Q. Doja and D. Prasad (*J. Indian Chem. Soc.*, 1942, **19**, 125—129; cf. A., 1941, II, 21).—*p*-NMe_2·C_6H_4·CHO and the respective α-picoline alkiodide give, with piperidine–EtOH, 2-p-*dimethylaminostyrylpyridine meth*-, m.p. 274°, *eth*-, m.p. 265°, *prop*-, m.p. 255—256°, and *but-iodide*, m.p. 245° (commercially, sensitin Z). Sensitisation spectra of the dyes are shown, and dyeing properties are examined. A. T. P.

Action of Grignard reagents on benzoylformanilides. R. F. Reeves and H. G. Lindwall (*J. Amer. Chem. Soc.*, 1942, **64**, 1086—1089).—BzCO·NPhEt and MgPhBr in boiling Et_2O–C_6H_6 give *N-ethylbenzilanilide*, OH·CPh_2·CO·NPhMe (75%), m.p. 97·5—98·5°, cyclised by Ac_2O, HCl–EtOH or $-H_2O$, cold conc. H_2SO_4, or, best, boiling 50% H_2SO_4 to 3 : 3-diphenyl-1-ethyloxindole, also obtained from 3 : 3-dichloro-1-ethyloxindole or CCl_3·CO·NPhEt by C_6H_6–$AlCl_3$ or from OAc·CPh_2·COCl (**I**) by NHPhEt. BzCO·NPhMe similarly gives *N-methylbenzilanilide* (81%), m.p. 106—107°, and thence (HBr–AcOH–H_2O) 3 : 3-diphenyl-1-methyloxindole, also obtained as above from (**I**) or 3 : 3-dichloro-1-methyloxindole. BzCO·NMe·C_6H_4·OEt-*p* gives *N*-methylbenzil-*p*-phenetidide (impure), b.p. 120—125°/2 mm. (decomp.), which with boiling HBr–EtOH–H_2O gives 5-*ethoxy*-3 : 3-*diphenyl*-1-*methyloxindole* (60%), m.p. 186·5—187·5°, also obtained from (**I**). β-$C_{10}H_7$·NHMe and (**I**) in boiling C_6H_6 give 3 : 3-*diphenyl*-1-*methyl*-β-*naphthoxindole* (71%), m.p. 253—254°. BzCO·NHPh and MgPhBr in Et_2O give *benzilanilide* (88%), m.p. 177—177·5°, whence red P–HI–AcOH yields $CHPh_2$·CO_2H and heating with $ZnCl_2$ at 185—190° gives 3 : 3-*diphenyloxindole*, m.p. 225—226°, also obtained from 3 : 3-dichloro-oxindole by C_6H_6–$AlCl_3$. R. S. C.

Separation of diketopiperazines and amino-acids in protein hydrolysates by ionophoresis. E. G. Antonovitsch and N. I. Gavrilov (*J. Gen. Chem. Russ.*, 1941, **11**, 763—764).—Serine, cystine, tryptophan (**I**), proline, and hydroxyproline pass towards the cathode more slowly than the acids previously studied (A., 1938, II, 351) and resemble dibasic NH_2-acids in this respect; thus, 50% of (**I**) passes towards the cathode in 103 hr.; the remaining acids require ~70 hr. ~8—10% undergo deamination. G. A. R. K.

Tetrahydroquinolines.—See B., 1942, II, 284.

Autoxidation phenomena of anils in the indandione (diketohydrindene) series. II. P. Pfeiffer and H. H. Roos (*J. pr. Chem.*, 1941, [ii], **159**, 13—35; cf. A., 1935, 1369).—β-Phenyl-β-*p*-tolylpropionyl chloride and $AlCl_3$–CS_2 afford 3-*phenyl*-6-*methyl*-1-*hydrindone* (**I**), m.p. 92—93° (not 3-*p*-tolyl-1-hydrindone; cf. von Braun *et al.*, A., 1929, 562), converted by HNO_3, *d* 1·1, at 190° in a sealed tube into benzophenone-2 : 4-dicarboxylic acid [Me_2 ester (**II**), m.p. 119—120°] or, by HNO_3, *d* 1·2, its (?-)NO_2-derivative (*Me_2* ester, m.p. 129°). (**II**) is synthesised by oxidation ($Na_2Cr_2O_7$–aq. H_2SO_4) of 2 : 4-$C_6H_3Me_2$·CH_2Ph, followed by esterification. (**I**) in aq. EtOH–NaOH is converted by PhNO into its 2-*anilo*-, m.p. 155° (and a *compound*, $C_{22}H_{11}O_2N$, m.p. 230°, after becoming orange at 205° and red at 225°), or by *p*-NO·C_6H_4·NMe_2 (in N_2) 2-p-*dimethylanilo*-derivative (**III**), m.p. 146°. (**III**) is oxidised (O_2) to 1-*hydroxy*-3 : 4-*diketo*-1-*phenyl*-2-p-*dimethylaminophenyl*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, m.p. 164—165°, converted (20% aq. NaOH) into 1-*keto*-3-*phenyl*-2-p-*dimethylaminophenyl*-6-*methyl*-1 : 3-*dihydroisoindole*, m.p. 267·5°. *p*-Tolylphthalide with NH_2Ph yields 1-*keto*-2-*phenyl*-, m.p. 190°, or with *p*-NH_2·C_6H_4·NMe_2, -2-p-*dimethylaminophenyl*-3-p-*tolyl*-1 : 3-*dihydroisoindole*, m.p. 229·5°. β-Phenyl-β-*m*-xylylpropionic acid, new m.p. 120—120·5°, gives a chloride, b.p. 180—184°/6 mm., which with $AlCl_3$–CS_2 affords 3-*phenyl*-4 : 6-*dimethyl*-1-*hydrindone*, m.p. 76·5—77°, and thence the 2-*anilo*-, m.p. 95—96° [with an *isomeride*, $C_{23}H_{19}ON$, m.p. 138° (structure suggested)], and 2-*dimethylanilo*-compound, m.p. 141·5—142° (with a *substance*, $C_{25}H_{24}O_2N_2$, m.p. 193°). β-Phenyl-β-*p*-anisylpropionic acid, new m.p. 77° (chloride, b.p. 176—182°/4 mm.), yields a ketone, b.p. 203°/6 mm., which affords the stereoisomeric α-, m.p. 166·5°, and β-*oximes*, m.p. 146·5°, both hydrolysed by HCl–EtOH to 6-*methoxy*-3-*phenyl*-1-*hydrindone*, m.p. 59° (2-*anil*, m.p. 130°). Its 2-*dimethylaminoanil*, m.p. 104—105°, is oxidised in EtOH by air to 1-*hydroxy*-3 : 4-*diketo*-6-*methoxy*-1-*phenyl*-2-p-*dimethylaminophenyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, m.p. 165°. A. T. P.

Electrolytic reduction of quinoline. V. V. Levtschenko (*J. Gen. Chem. Russ.*, 1941, **11**, 686—690).—A suspension of quinoline (**I**) in 9% aq. KOH is electrolysed using a Hg cathode and a Pt anode, at 14 amp. per sq. dm./13 v., giving monomeric *dihydroquinoline* (**II**), m.p. 199—200° (yield 3%) together with tetrahydroquinoline (**III**) (0·1%) and unchanged (**I**). Reduction of (**I**) in an acid medium affords the di- and tri-merides of (**II**). Reduction of (**II**) with Sn and HCl gives (**III**). G. A. R. K.

Reaction of ethyl acetoacetate with *p*-aminoacetanilide. G. Jacini (*Gazzetta*, 1941, **71**, 53—57).—*p*-NH_2·C_6H_4·NHAc (**I**) and excess of CH_2Ac·CO_2Et (**II**) in boiling *o*-C_6H_4Me·NO_2 give p-(*acetamido*)*acetoacetanilide*, m.p. 163—164°. At 100° (bath), (**I**) and (**II**) give *Et* β-p-*acetamidoanilinocrotonate*, m.p. 182°, which at 270° (bath) gives 4-*hydroxy*-, m.p. 358°, converted by $POCl_3$ into 4-*chloro*-6-*acetamido*-2-*methylquinoline*, m.p. 206—208°. This is hydrolysed to 4-*chloro*-6-*amino*-, m.p. 170—171°, and converted by MeOH–NaOMe at 130—140° into 6-*acetamido*-4-*methoxy*-2-*methylquinoline*, m.p. 190°. E. W. W.

Quinoline- and quinaldine-6-sulphonamide from sulphanilamide. G. V. Tschelincev and V. N. Zakotin (*J. Gen. Chem. Russ.*, 1941, **11**, 729—730).—*p*-NHAc·C_6H_4·SO_2·NH_2 yields by the Skraup reaction *quinoline*-6-*sulphonamide*, m.p. 191—192° (30%), and by the Doebner–Miller reaction, quinaldine-6-sulphonamide, m.p. 212—213° (36%). G. A. R. K.

Derivatives of amino*iso*quinolines. J. J. Craig and W. E. Cass (*J. Amer. Chem. Soc.*, 1942, **64**, 783—784).—4-Bromo- (modified prep.), m.p. 38—39° (*picrate*, m.p. 195·5—197°), with aq. NH_3–$CuSO_4$ at 165—170° gives 4-amino-*iso*quinoline (70%), m.p. 108·5° [*picrate*, m.p. 231—232·5° (decomp.)], and thence 4-*acet*-, m.p. 167—168°, 4-*benz*-, m.p. 188—189°, and 4-N^4-*acetylsulphanil*-, m.p. 304—306° (decomp.), hydrolysed by boiling 12% HCl to 4-*sulphanilamidoisoquinoline* (**I**), m.p. 211·5—212·5°. 5- (prep. from the NO_2-compound by H_2–Raney Ni in abs. EtOH at 3 atm.), m.p. 128—129° (*Ac*, m.p. 166°, and *Bz* derivative, m.p. 158—159°), and 1-amino*isoquinoline* (*Ac*, m.p. 148—148·5°, and *Bz*$_2$ derivative, m.p. 223·5—224·5°) give 5-, m.p. 284—288° (decomp.), and 1-N^4-*acetylsulphanil*-, m.p. 246—247°, and thence by acid 5- (**II**), m.p. 223—224·5° (decomp.), and by alkali 1-*sulphanil-amido*isoquinoline (**III**), m.p. 264—267° (decomp.). (**III**) is as effective as sulphadiazine against streptococci (mice), (**I**) less so, and (**II**) ineffective. At 5—20 mg. per 20 g. body wt. only (**II**) is toxic to mice. R. S. C.

Acridines.—See B., 1942, II, 281.

Tautomeric character of the glyoxaline ring. H. Green and A. R. Day (*J. Amer. Chem. Soc.*, 1942, **64**, 1167—1173).—The theory of Roeder *et al.* (A., 1941, II, 150) as to the mode of formation of benziminazoles is confirmed. The tautomerism of glyoxalines is not explained by either prototropy or electromerism alone. 3 : 1 : 4-[prep. from 3 : 1 : 4-NO_2·C_6H_3Me·NH_2 (**I**) by Ac_2O and then H_2–Pd–C in EtOH] (*hydrochloride*, m.p. 228—230°) and 4 : 1 : 3-NH_2·C_6H_3Me·NHAc (similarly prepared), m.p. 84·9—85·5° (*hydrochloride*, m.p. 144—145°), when heated alone above the m.p. (N_2) or in boiling *p*-cymene (**II**) or 4N-HCl, gives 2 : 5(6)-dimethylbenziminazole (**III**), which is obtained from 1 : 3 : 4-$C_6H_3Me(NHAc)_2$ only at 211—213° (N_2). *m*-C_6H_4Me·NHAc and HNO_3 (*d* 1·5) in AcOH–Ac_2O at <10° give 4 : 1 : 3- (**IV**) (36%) and 6 : 1 : 3-NO_2·C_6H_3Me·NHAc, separated after hydrolysis by 1 : 1 H_2SO_4–H_2O at 100°. 3 : 1 : 4-NH_2·C_6H_3Me·NMeAc [prep. from (**I**)] and 3-*acetmethylamido*-p-*toluidine*, m.p. 142—142·5° [prep. from (**IV**) by way of its p-C_6H_4Me·SO_2 derivative, m.p. 136—137°, p-*toluenesulphon*-*N*-*methyl*-4-*nitro*-m-*toluidide*, m.p. 89·3—90·3°, and finally by hydrolysis and hydrogenation], are unchanged in boiling (**II**). Hydrogenation (Pd–C) of 3 : 1 : 4-NO_2·C_6H_3Me·NHMe in EtOH gives 3 : 1 : 4-NH_2·C_6H_3Me·NHMe, unstable [dihydrochloride, softens at 80°, m.p. 147° (cf. lit.)], and thence (Ac_2O–$NaHCO_3$–Et_2O) 3 : 1 : 4-NHAc·C_6H_3Me·NHMe (**V**); similarly are obtained 4 : 1 : 3-NH_2·C_6H_3Me·NHMe, unstable, and its *dihydrochloride*, decomp. 190°, and 4-*Ac* derivative (**VI**), m.p. 74—78°. Ring-closure of (**V**) and (**VI**) to 1 : 2 : 6-trimethylbenziminazole is readily effected in boiling C_6H_6 or PhMe. 3 : 1 : 4- and 4 : 1 : 3-NH_2·C_6H_3Me·NHBz, m.p. 97—98° (lit. 83°), in boiling (**II**) or 4N-HCl or when heated above the m.p. give 2-phenyl-5(6)-methylbenziminazole (**VII**), m.p. 249—250° (lit. 240°). *Benzylidene*-4-*acetamido*-m-, m.p. 74—78°, and -3-*acetamido*-p-*toluidine* (prep. from NH_2·C_6H_3Me·NHAc by PhCHO in EtOH), m.p. 122—123°, are simultaneously hydrolysed and oxidised to (**VII**) by KOH–EtOH–$PhNO_2$ at 100°. R. S. C.

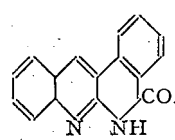
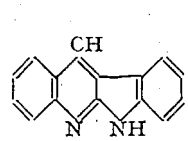
Pyrrole series. VII. Synthesis of unsymmetrical *N*-methyldipyrrylmethanes. W. M. Quattlebaum, jun., and A. H. Corwin (*J. Amer. Chem. Soc.*, 1942, **64**, 922—925; A., 1941, II, 338).—*Et* 1 : 4-*dimethyl*-2-*bromomethylpyrrole*-3 : 5-*dicarboxylate* (**I**) (prep. from the Me_3 compound by Br–AcOH at 30—40°), m.p. 82°, with the appropriate substituted pyrrole and a drop of HCl in boiling MeOH gives 3 : 5 : 4′-*tricarbethoxy*-1 : 4 : 3′ : 5′-*tetra*- (75%), m.p. 110°, and 3′-*bromo*-3 : 5 : 5′-*tricarbethoxy*-1 : 4 : 4′-*tri*-*methyldipyrrylmethane* (62%), m.p. 142°, and *Et* 3 : 5 : 5′-*tricarbethoxy*-1 : 4 : 4′-*trimethyldipyrrylmethane*-3-*propionate* (70%), m.p. 114°. Cryptopyrrole does not condense with (**I**), but the derived MgBr derivative gives 3 : 5-*carbethoxy*-1 : 4 : 3′ : 5′-*tetramethyl*-4′-*ethyldipyrrylmethane* (56%),

m.p. 126°. Replacement of (I) by *Et 5-carbethoxy*-1 : 4-*dimethyl*-2-*bromomethylpyrrole*-3-*propionate* (II) causes all condensations to fail. The reaction is thus greatly influenced by the nature of substituents in either component. Et 3-bromo-2 : 4-dimethylpyrrole-5-carboxylate with Br–AcOH and then SO_2Cl_2 at 14° and later 0·2° and finally H_2O at, first 0°, and then 60° gives 3-*bromo*-5-*carbethoxy*-4-*methylpyrrole*-2-*carboxylic acid* (40% + some aldehyde), m.p. 254° (decomp.), decarboxylated in glycerol to *Et* 3-*bromo*-4-*methylpyrrole*-5-*carboxylate* (40%), m.p. 179—183° (decomp.). Et 1 : 2 : 4-trimethylpyrrole-5-carboxylate with anhyd. HCN–HCl–Et_2O and later H_2O at 40° gives the 3-*CHO* derivative, m.p. 63—64° (also obtained by methylation of Et 3-formyl-2 : 4-dimethylpyrrole-5-carboxylate), converted by $CH_2(CO_2H)_2$–NH_2Ph in boiling EtOH into β-5-*carbethoxy*-1 : 2 : 4-*trimethyl*-3-*pyrrylacrylic acid* (68%), m.p. 184—189°, which with 3% Na–Hg in H_2O gives β-5-*carbethoxy*-1 : 2 : 4-*trimethyl*-3-*pyrrylpropionic acid*, m.p. 153—154°, and thence (Br–AcOH; room temp.) (II), m.p. 158° (decomp.). Et 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate with $CMe_2Et{\cdot}ONa$–$CMe_2Et{\cdot}OH$–Me_2SO_4 gives the 1 : 2 : 4-Me_3 compound (80%), m.p. 60°, reduced to the 3-Et compound, which with Br gives oils. Prep. of 5-carbethoxy-1 : 4-dimethyl-3-ethylpyrrole-2-carboxylic acid, m.p. 149—150° (slight decomp.), and *N*-methylation [$CMe_2Et{\cdot}ONa$–$CMe_2Et{\cdot}OH$–Me_2SO_4 or K salt + Me_2SO_4; product, b.p. 215—221° (bath)] of methylethylmalcimide are improved. R. S. C.

Pyrimidines. CLXXVII. Synthesis of derivatives of pyrimidine-5-carboxylic acid. (Miss) E. Ballard and T. B. Johnson (*J. Amer. Chem. Soc.*, 1942, **64**, 794—798; cf. A., 1942, II, 272).—Addition of $CS(NH_2)_2$ and then of $OEt{\cdot}CH{:}C(CO_2Et)_2$ (I) to NaOEt–EtOH and heating gives *Et* 6-*hydroxy*-2-*thiolpyrimidine*-5-*carboxylate* (85%), m.p. 245°, converted by hot, aq. $CH_2Cl{\cdot}CO_2H$ into uracil-5-carboxylic acid (II), also obtained with a little *Et* 6-*hydroxypyrimidine*-5-*carboxylate*, m.p. 185° after sintering, by H_2O_2–H_2SO_4–H_2O.
$CH_2Ph{\cdot}S{\cdot}C(:NH){\cdot}NH_2$ gives similarly *Et* 6-*hydroxy*-, m.p. 174—179°, and thence ($POCl_3$) *Et* 6-*chloro*-, b.p. 248°/11 mm., -2-*benzylthiol*-*pyrimidine*-5-*carboxylate*. Condensation of (I) with $NH_2{\cdot}C(:NH){\cdot}SO_2H$ is unsatisfactory, but in aq. KOH (2 equivs.) gives 10% of *Et*$_2$ *carbamidomethylenemalonate*, m.p. 207—212°. Chlorination of the Me ester of (II) is difficult, but PCl_5–$POCl_3$ gives a little Me 2 : 6-dichloro- and thence (conc. aq. NH_3) *Me* 2-*chloro*-6-*amino*-*pyrimidine*-5-*carboxylate*, m.p. 159—161°. Et 6-chloro-2-ethylthiolpyrimidine-5-carboxylate (improved prep.) is dehalogenated in 40—50% yield by Zn dust in boiling EtOH, but the method fails with the 2 : 6-Cl_2-compound (III). Red P–HI–AcOH reduces (III) to 6-*hydroxy*-*pyrimidine*-5-*carboxylic acid*, decomp. variable, 220° to 250° (decarboxylation at 250°). Et 2-ethylthiolpyrimidine-5-carboxylate (IV) and Cl_2–H_2O at 40—70° give *Et* 2-*chloro*- (V) (79%), m.p. 61°, and some *Et* 2-*ethylsulphonyl*-*pyrimidine*-5-*carboxylate*, m.p. 87—89°. NH_3–H_2O or –EtOH at 100° has no effect on (IV), but NH_3–EtOH and (V) give *Et* 2-*aminopyrimidine*-5-*carboxylate*, m.p. 147—149°, and thence the *acid*, m.p. >300°. R. S. C.

Pyridine series. V. Reactions involving the *ortho* effect in certain βγ-substituted pyridines. M. J. Reider and R. C. Elderfield (*J. Org. Chem.*, 1942, **7**, 286—296).—Et 5-cyano-6-hydroxy-2-methyl*iso*nicotinate is converted by PCl_5 in $POCl_3$ into *Et* 6-*chloro*-5-*cyano*-2-*methyl*iso*nicotinate* (I), b.p. 135—136·5°/0·5 mm., m.p. 62°, converted by H_2–Pd–$BaCO_3$ in EtOH into *Et* 5-*cyano*-2-*methyl*iso*nicotinate* (II), m.p. 58° [corresponding *amide* (III), m.p. 275° (decomp.)]. (I) and aq. NH_3 at room temp. give 6-*chloro*-5-*cyano*-2-*methyl*iso*nicotinamide* (IV), m.p. 233°. The Hofmann degradation of (III) leads to *dihydroxymethylcopazoline* [3 : 6-*dihydroxy*-6′-*methylpyrido*-3′ : 4′-4 : 5-*pyrimidine*], m.p. >310° (yield 70%), and 4 : 5-*diamino*-2-*methylpyridine* [*dihydrochloride*, m.p. >250° (decomp.)]. (IV) is very readily hydrolysed by 6N-HCl at room temp. to 6-*chloro*-5-*cyano*-2-*methyl*iso*nicotinic acid* (V), m.p. 198·5° (*Me* ester, m.p. 168·5°), also obtained by the alkaline hydrolysis of (I). Boiling 5% HCl and (V) yield 6-*chloro*-2-*methylcinchomeronic acid*, m.p. 205° (*Me*$_2$ ester, m.p. 85°). (II) is very readily hydrolysed by alkali to 5-*cyano*-2-*methyl*iso*nicotinic acid*, m.p. 230°, also obtained from (III) and cold 0·1N-HCl; it is decarboxylated by Cu powder to 5-*cyano*-2-*methylpyridine*, m.p. 84—85°; 6-*chloro*-5-*cyano*-2-*methylpyridine*, m.p. 114·5—115·5°, is obtained analogously. (IV) and Br in MeOH give the *bromoamide*, m.p. 199·8°, which does not appear to rearrange with NaOMe in boiling MeOH. (II) and N_2H_4 in EtOH–Et_2O (1 : 1) yield 3-*amino*-6-*hydroxy*-6′-*methylpyrido*-3′ : 4′-4 : 5-*pyridazine*, m.p. 324° (*hydrochloride*), which does not form a derivative with PhCHO. Under similar conditions (I) affords 6-*chloro*-5-*cyano*-2-*methyl*iso*nicotinhydrazide*, sublimes at >360° (:*CHPh* derivative, m.p. 282·5°). (V) and boiling $SOCl_2$ yield 6-*chloro*-5-*cyano*-2-*methyl*iso*nicotinyl chloride*, m.p. 98—103°. (I) is reduced (H_2–Pd–NaOAc–AcOH) to *Et* 2-*methyl*-5-*aminomethyl*iso*nicotinate* [*picrate*, m.p. 170° (decomp.)] and 2-*hydroxy*-6′-*methylpyrido*-3′ : 4′-4 : 3-*pyrrolenine*, m.p. 250° in sealed tube (*picrate*, m.p. 205·5°; *hydrochloride*, sublimes >285°). M.p. are corr. H. W.

Polynuclear condensed systems with heterocyclic rings. XIII. Polycyclic systems from 2-aminobenzylideneaniline. W. Borsche, M. Wagner-Roemmich, and J. Barthenheier (*Annalen*, 1942, **550**, 160—174; cf. A., 1939, II, 87).—2-$NH_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4Me$-4′ (I), 4 : 6-dihydro-5 : 5-dimethyl- (II) or -5-phenyl-resorcinol, and piperidine at 100° (bath) afford 4-*keto*-2 : 2-*dimethyl*-, m.p. 118° (*picrate*, m.p. 198—199°; 2 : 4-*dinitrophenylhydrazone*, m.p. 301°; *semicarbazone*, m.p. 236°), or -2-*phenyl*-1 : 2 : 3 : 4-*tetrahydroacridine*, m.p. 158°, respectively. 1 : 4-Diketo*cyclo*hexane (*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 240°) similarly yields 2 : 3 : 6 : 7-*dibenzo*-9 : 10-*dihydro*-1 : 8-*diazaphenanthrene*, m.p. 256—257°; 1 : 3 : 5-$C_6H_3(OH)_3$ gives 2 : 3 : 6 : 7-*dibenzo*-9-*keto*-9 : 10-*dihydro*-1 : 5-*diazaphenanthrene*, m.p. >360°, converted by warm AcOH–HNO_3 (*d* 1·4) into 2 : 3 : 6 : 7-*dibenzo*-1 : 5-*diazaphenanthrenequinone*. (II) and *o*-$NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H$ in MeOH yield γ-2-(4-*carboxyquinolino*)-ββ-*dimethylbutyric acid*, m.p. 156—157°. Barbituric acid and (I) or its 4 : 5-$(OMe)_2$-derivative (III) with piperidine afford 2 : 4-*diketo*-1 : 2 : 3 : 4-*tetrahydro*-1 : 3-*diaza*-*acridine*, m.p. 368°, or its 6 : 7-(*OMe*)$_2$-derivative, m.p. 358—360°, respectively. Homophthalimide and (I) or (III) or *o*-aminopiperonylidene-*p*-toluidine (IV) in piperidine–$C_5H_{11}{\cdot}OH$ give 2 : 3 : 5 : 6-dibenzo-7-keto-7 : 8-dihydro-1 : 8-naphthyridine (V), new m.p. 262°, or its 2′ : 3′-(*OMe*)$_2$-, m.p. 330—332° (*picrate*, m.p. 286—288°), or -CH_2O_2-derivative, m.p. 340°, respectively. (I) and oxindole (VI) with piperidine at 150° yield quinindoline (VII), whereas (I) and (VI) in aq. NaOH–EtOH afford 2-*aminobenzylideneoxindole*, m.p. ~230° (*Ac*$_2$ derivative, m.p. 221—222°), also obtained from the corresponding 2-NO_2-compound, m.p. 227—229°, and $SnCl_2$–HCl, and convertible by heat into (VII). (V) and (III) or (IV) + piperidine at 150° yield 7 : 8-*dimethoxy*-, m.p. 302° (10-*Ac* derivative, m.p. 223°), or 7 : 8-*methylenedioxy*-*quinindoline*, m.p. 305—315° (10-*Ac* derivative, m.p. 217—219°), respectively, also obtained

(V.)  (VII.) 

by heating (170—180°) 6-*aminoveratrylideneoxindole*, m.p. 110—115° (*Ac*$_2$ derivative, m.p. 242—243°) (prepared from the 6-NO_2-compound, m.p. 261°), or 6-aminopiperonylideneoxindole (*Ac*$_2$ derivative, m.p. 221—222°), respectively. 1-Methyloxindole and *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$–EtOH–piperidine (boil for 2 days) give 3-(2′-*nitrobenzylidene*)-1-*methyloxindole*, m.p. 258—259°, reduced to the 2-NH_2-compound, m.p. 245—247° (convertible by boiling $C_5H_{11}{\cdot}OH$–glycerol–piperidine into 11-methylquinindoline). 3-(6′-*Aminoveratrylidene*)-, m.p. 208—209° (*Ac* derivative, m.p. 253—255°), and -*piperonylidene*)-1-*methyloxindole*, m.p. 315—316° (*Ac* derivative, m.p. 284—285°), are prepared. A. T. P.

Mechanism of the chemiluminescence of 3-aminophthalhydrazide. H. Kautsky and K. H. Kaiser (*Naturwiss.*, 1942, **30**, 148).—Treatment of the hydrazide (I) in pure $COMe_2$ with $Ca(OCl)_2$ gives a violet-red solution with all the properties of an azodiacyl compound (II). Addition of dil. aq. alkali to this solution causes a short, bright blue luminescence. After hydrolysis of (II) the decolorised solution contains (I) and therefore gives a temporary luminescence after addition of a suitable oxidising agent. The course of the change is:

$$(I) \rightarrow NH_2{\cdot}C_6H_3\langle \begin{matrix} CO{\cdot}N \\ CO{\cdot}N \end{matrix} \rangle \rightarrow 3 : 2 : 1\text{-}NH_2{\cdot}C_6H_3(CO_2H)_2 + NH{:}NH \rightarrow$$

$$\left[NH_2{\cdot}C_6H_3\langle \begin{matrix} CO{\cdot}NH \\ CO{\cdot}NH \end{matrix} \rangle\right]^* + N_2 \rightarrow (I) + h\nu.$$

H. W.

Comparative reactivity of the carbonyl groups in the thionaphthenquinones. I. Constitution of certain thioindigoid dyes. J. Harley-Mason and F. G. Mann (*J.C.S.*, 1942, 404—415).—The factors determining the type of condensation of the thioindoxyls with the thionaphthenquinones (I) (*i.e.*, whether the CH_2 of the former reacts with the α-CO of the latter to give a thioindigo or with the β-CO to give a thioindirubin) have been investigated. For this purpose, thioindoxyl (II) and six substituted (II) have been condensed with the corresponding (I), and the product in each case compared with that obtained by the condensation of the (II) with the corresponding α-anil, where α-condensation must necessarily have occurred. As the compounds obtained have high or indefinite m.p. the identity of pairs of compounds has been determined by the following means: reductive acetylation (Zn–AcOH–Ac_2O) to a diacetyldihydro-derivative, *X*-ray analysis by the " powder " method, alkali fission in a few cases, dyeing tests on cotton, and, as confirmatory test, colours of H_2SO_4 solutions. The results show that the condensation in most cases is determined solely by the position of substituents in the quinone mol. and is unaffected by those in the thioindoxyl mol. Thionaphthenquinone and 5- or 6-substituted (I) always give β-condensation, 4-substituted (I) always give α-condensation, and 7-substituted (I) may give α- or β-condensation; only with the last quinones is the type of condensation affected by the (II) employed. Indoxyl and oxindole always give β- and α-condensation respectively with all the (I), the effect of the two compounds being to suppress completely the influence of substituents in the quinone mol. The significance of the results is discussed.

The following are described (temp. in parentheses are the m.p. of the *diacetyldihydro*-derivative): 3-*carboxynaphthyl*-2-*thioglycollic acid*, m.p. 175—176°, from Na 2-thiol-3-naphthoate and $CH_2Cl{\cdot}CO_2H$; 6-

ethoxythionaphthenquinone-2-p-*hydroxyanil*, m.p. 237—239°, from *p*-NO·C_6H_4·OH and 5-chloro-7-methylthioindoxyl, and the 5 : 6-*benz*-compound, m.p. 280—282° (decomp.); 6-*chloro*-4-*methylthioindirubin* (144—145°), 6-*chloro*-4-*methylthioindigo* (182—183°), 6-*ethoxylthioindirubin* (131—133°), 6-*ethoxythioindigo* (162—165°), 4 : 5-*benzthioindirubin* (162—163°), 4 : 5-*benzthioindigo* (214—217°), 5 : 6-*benzthioindirubin*, 5 : 6-*benzthioindigo* (254—256°), 6 : 7-*benzthioindirubin* (178—179°), 6 : 7-*benzthioindigo* (254—256°), 5 : 6′-*dichloro*-4 : 4′-*dimethylthioindigo* (290—292°); 6′-*chloro*-6-*ethoxy*-4′-*methylthioindigo* (178—182°), 6′-*chloro*-4′-*methyl*-4 : 5-*benzthioindigo* (196—199° (decomp.)], 6′-*chloro*-4′-*methyl*-6 : 7-*benzthioindigo* [252—253° (decomp.)], 6′-*chloro*-4′-*methyl*-5 : 6-*benzthioindigo* (261—263°), 5-*chloro*-7-*methylthioindigo* (213—215°), 5 : 5′-*dichloro*-7 : 7′-*dimethylthioindigo* (308—310°), 5-*chloro*-6′-*ethoxy*-7-*methylthioindigo* (214—216°), 5′-*chloro*-7′-*methyl*-4 : 5- (269—272°), -6 : 7- (235—238°), and -5 : 6-*benzthioindigo* (258—260°), 5′-*chloro*-7′-*methyl*-6 : 7-*benzthioindirubin* (167—169°), 6-*chloro*-6′-*ethoxy*-4-*methylthioindirubin* (138—140°), 5-*chloro*-6′-*ethoxy*-7-*methylthioindirubin* (148—149°), 6 : 6′-*diethoxythio-indirubin* (144—146°) and -*indigo* (230—232°, 6′-*ethoxy*-6 : 7-*benzthio-indirubin* (166—169°) and -*indigo* (205—208°), 6′-*ethoxy*-5 : 6-*benzthio-indirubin* and -*indigo* [224—225° (decomp.)], 6′-*ethoxy*-4 : 5-*benzthioindigo* (221—225°), 4 : 5 : 4′ : 5′-*dibenzthioindigo* (>315°), 4 : 5 : 6′ : 7′-*dibenzthioindigo* (254—257°), 4 : 5 : 5′ : 6-*dibenzthioindigo* (263—265°), *ethoxy*-6′ : 7′-*benzthioindirubin* (162—165°), 4 : 5—6′ : 7′-*dibenzthioindirubin* (227—230°), 6 : 7 : 6′ : 7′-(>315°) and 5 : 6 : 6′ : 7′-*dibenzthioindigo* (251—253°), 5-*chloro*-7-*methyl*-, 6-*ethoxy*-, 4 : 5-, 6 : 7-, and 5 : 6-5′ : 6′-*dibenzthioindirubin*, and 5 : 6 : 5′ : 6′-*dibenzthioindigo* [297—300° (decomp.)]; 3-(6-*chloro*-4-*methylthionaphthen*)-2′-*indole-indigo*, 6-*chloro*-4-*methylthiooxindole*-3-*aldehydephenylhydrazone*, m.p. 167—169°; 3-(5-*chloro*-7-*methylthionaphthen*)-2′-*indole-indigo* (-*aldehyde*, m.p. 116—118°, and *phenylhydrazone*, m.p. 194—196°), 3-(6-*ethoxy*)- (6-*ethoxy-aldehyde*, m.p. 152—154°), 3-(4 : 5-*benz*)- (4 : 5-*benz-aldehyde*, m.p. 144—145°), 3-(6 : 7-*benz*)- (*aldehyde phenylhydrazone*, m.p. 220—222°), and 3-(5 : 6-*benz*)-derivatives (5 : 6-*benz-aldehyde*, m.p. 145—146°); 2-(6-*chloro*-4-*methylthionaphthen*)-2′-*indole-indigo* (6-*chloro*-4-*methylthioindoxyl*-2-*aldehydephenylhydrazone*, m.p. 153—154°, 2-(5-*chloro*-7-*methyl*), 2-(6-*ethoxy*)-, 2-(4 : 5-*benz*)- (4 : 5-*benz-aldehyde*, m.p. 131—132°), 2-(6 : 7-*benz*)- (*aldehyde phenylhydrazone*, m.p. 197—200°), and 2-(5 : 6-*benz*)-derivatives (5 : 6-*benz-aldehyde*, m.p. 137—139°); 2-(6-*chloro*-4-*methylthionaphthen*)-3′-*indole-indigo*, 2-(5-*chloro*-7-*methyl*)-, 2-(6-*ethoxy*)-, 2-(4 : 5-*benz*)-, 2-(6 : 7-*benz*)- and 2-(5 : 6-*benz*)-derivatives; 2-*acetamido*-1-*naphthylthioglycollic acid*, m.p. 185°, and the 2-*Cl-acid*, m.p. 95—97°. F. R. S.

1 : 3 : 5-Triazines.—See B., 1942, II, 316.

Bile pigments. XXXIV. New preparation of hydroxypyrromethenes by alkaline condensation of hydroxypyrroles with pyrrole-α-aldehydes and further attempted synthesis of acetyl-substituted bile pigments; tripyrrenes. H. Plieninger and H. Lichtenwald (*Z. physiol. Chem.*, 1942, **273**, 206—224).—Condensation of the mixture (**I**) of hydroxyopsopyrroles (obtained by the oxidation of opsopyrrole with H_2O_2) with 2-formyl-3-methylpyrrole-4-propionic acid in alkaline solution yields a mixture from which, after esterification, Me *iso*-neoxanthobilirubate, m.p. 201°, is isolated. Similar condensations lead to coproneoxanthobilirubic acid and *Me* 5-*hydroxy*-4′-*acetyl*-4 : 3′ : 5′-*trimethylpyrromethene*-3-*propionate*, m.p. 218°. (**I**) and 2-formyl-4-methyl-3-bromovinylpyrrole-5-carboxylic acid yield a mixture of 5-hydroxy-4 : 4′-dimethyl-3-ethyl-3′-bromovinyl- and 5-hydroxy-3 : 4′-dimethyl-4-ethyl-3′-bromovinyl-pyrromethene-5′-carboxylic acid, m.p. >300°, darkens at 230°. Oxidation of 3-methylpyrrole by H_2O_2 in C_5H_5N affords 2-*hydroxy*-3(or 4)-*methylpyrrole* (**II**), b.p. ~145°/12 mm., m.p. 84°, from which *Me* 5-*hydroxy*-3 (or 4) : 3′-*dimethylpyrromethene*-4′-*propionate*, m.p. 183°, is derived; this is converted by successive treatments with CH_2O and HCl in MeOH, $FeCl_3$, and NaOH into *Me*$_2$ 1′ : 8′-*dihydroxy*-1(or 2) : 3 : 6 : 7 (or 8)-*tetramethylbilitriene*-4 : 5-*dipropionate*, m.p. 210°. (**II**) is condensed with 5-formyl-2 : 4-dimethylpyrrole-3-propionic acid to *Me* 5-*hydroxy*-3′ : 3(or 4) : 5-*trimethylpyrromethene*-4′-*propionate*, decomp. 278°, with cryptopyrrolcaldehyde to 5-*hydroxy*-3′ : 3(or 4) : 5′-*trimethyl*-4′-*ethylpyrromethene*, m.p. 223°, with 5-formyl-3-acetyl-2 : 4-dimethylpyrrole to 5-*hydroxy*-4′-*acetyl*-3′ : 3(or 4) : 5′-*trimethylpyrromethene*, m.p. 307°, and with 2-formyl-4-acetyl-3-methylpyrrole to 5-*hydroxy*-4′-*acetyl*-3′ : 3(or 4)-*dimethylpyrromethene*, m.p. 260—262°, converted by PhN_2Cl followed by $Cu(OAc)_2$ into the *Cu* salt of 5-*hydroxy*-4′-*acetyl*-3′ : 3(or 4)-*dimethylpyrromethene*-5′-*azobenzene*, m.p. >300°. 5-*Hydroxy*-4′-*acetyl*-3′ : 4-*dimethylpyrromethene*-3-*propionic acid*, m.p. 263°, is converted into the *Cu* salt of *Me* 5-*hydroxy*-4′-*acetyl*-3′ : 4-*dimethylpyrromethene*-3-*propionate*-5′-*azobenzene*, m.p. >290°, which is reduced by Zn dust in AcOH to *Me* 5′-*amino*-5-*hydroxy*-4′-*acetyl*-3′ : 4-*dimethylpyrromethene*-3-*propionate*, m.p. 286°. Me neoxanthobilirubate (**III**) is condensed (HBr in cold MeOH) with 5-formyl-3-methyl-4-ethylpyrrole to *Me* 1′-*hydroxy*-1 : 3 : 6-*trimethyl*-2 : 5-*diethyltripyrryl*-2′α : 4′β-*diene*-4-*propionate*, m.p. 143° (Kofler), which gives a red fluorescence and characteristic spectrum after addition of $Zn(OAc)_2$ in MeOH. Similarly (**III**) and Me 5-formyl-3-methyl-4-ethylpyrrole-2-carboxylate give *Me* 1′-*hydroxy*-6′-*carboxy*-1 : 3 : 6-*trimethyl*-2 : 5-*diethyltripyrryl*-2′α : 4′β-*diene*-4-*propionate* (**IV**), m.p. 208—214° (Kofler). Analogous condensations lead from (**III**) to *Me* 1′-*hydroxy*-6-*carboxy*-1 : 3 : 6-*trimethyl*-2-*ethyl*-5-*bromovinyltripyrryl*-2′α : 4′β-*diene*-4-*propionate*, no definite m.p. (*Ca* salt), and Me 1′-hydroxy-6′-carboxy-1 : 3 : 6-trimethyl-2 : 5-diethyltripyrryl-2′α : 4′α-diene-4-propionate (*Ca* salt). (**III**) and Me 5-formyl-3-methyl-4-ethylpyrrole-2-carboxylate afford *Me* 1′-*hydroxy*-6′-*carbomethoxy*-1 : 3 : 6-*trimethyl*-2 : 5-*diethyltripyrryl*-2′α : 4′β-*diene*-4-*propionate* (**V**), m.p. 166—168°. Analogously obtained are *Me* 1′-*hydroxy*-6′-*carbomethoxy*-1 : 3 : 6-*trimethyl*-2-*ethyl*-5-*bromovinyltripyrryl*-2′α : 4′β-*diene*-4-*propionate* and *Me* 1′-*hydroxy*-1(or 2) : 4 : 5-*trimethyl*-2(or 1) : 6-*diethyl*-4-*bromovinyltripyrryl*-2′α : 4′β-*diene*-6′-*carboxylate*, m.p. 183°. (**IV**) is not esterified by HCl in boiling MeOH but is converted into a red *pigment*, m.p. 115°. (**V**) is converted by $Zn(OAc)_2$ and $Cu(OAc)_2$ into the *salts*, $C_{27}H_{31}O_5N_3Zn$ and $C_{27}H_{31}O_5N_3Cu$. (**V**) is reduced by Zn dust in AcOH to *Me* 1′-*hydroxy*-6′-*carbomethoxy*-1 : 3 : 6-*trimethyl*-2 : 5-*diethyltripyrryl*-2′α-*ene*-4-*propionate*, m.p. 230° (Kofler). Me neobilirubinate and Me 5-formyl-3-methyl-4-ethylpyrrole-2-carboxylate condense to *Me* 1′-*hydroxy*-6′-*carbomethoxy*-1 : 3 : 6-*trimethyl*-2 : 5-*diethyltripyrryl*-5′β-*ene*-4-*propionate*, m.p. 150° (Kofler). Neoxanthobilirubic acid and 2-formyl-4-acetyl-3-methylpyrrole yield *Me* 1-*hydroxy*-6-*acetyl*-1 : 3 : 5-*trimethyl*-2-*ethyltripyrrene*-4-*propionate*, m.p. 128° (*hydrobromide*, m.p. >300°). H. W.

5-Pyrazolylacetylene and 5 : 5′-dipyrazolyl. R. Kuhn and K. Henkel (*Annalen*, 1941, **549**, 279—285).—$(CH{:}C)_2$ and CH_2N_2 in Et_2O give in 1—2 days 5-*pyrazolylacetylene* (**I**) (40—50%), m.p. 45—46° [*picrate*, m.p. 122—124° (block), 126—127·5° (micro)], and after ~3 weeks also 5 : 5′-*dipyrazolyl* (**II**) (yield variable; >35%), m.p. 255—256° (block), sublimes [also obtained from (**I**) and CH_2N_2]. (**I**) gives Cu and Ag salts and is hydrogenated (PtO_2; Et_2O; ~20°) to 5-*ethylpyrazole* (**III**), b.p. ~90° (bath)/12 mm. (*picrate*, m.p. 128·5—129·5°). 5-Vinylpyrazoline (**IV**) (Müller *et al.*, A., 1932, 754) with H_2–PtO_2 in Et_2O gives 5-*ethylpyrazoline*, b.p. 59—61°/15 mm., which with Br– or $Pb(OAc)_4$–$CHCl_3$ gives (**III**), thereby proving the structure of (**III**) and (**I**). Attempts to obtain (**III**) from $(CH_2{:}CH)_2$ or (**IV**) by way of 5 : 5′-dipyrazolinyl failed owing to poor yields of the latter. R. S. C.

Enzymic degradation and structure of nucleic acids.—F. G. Fischer (*Naturwiss.*, 1942, **30**, 377—382).—A review.

Enzymic hydrolysis of ribonucleic acid and its relation to structure.—See A., 1942, III, 777.

Synthesis of biliverdin (uteroverdin) and bilirubin. H. Fischer and H. Plieninger (*Naturwiss.*, 1942, **30**, 382—387).—A review.

Light absorption and constitution of chlorophyll derivatives. II.—See A., 1942, **I**, 314.

Morpholinoalkyl esters and amides possessing antispasmodic activity. L. C. Cheney and W. G. Bywater (*J. Amer. Chem. Soc.*, 1942, **64**, 970—973).—Morpholine and Cl·$[CH_2]_n$·Cl give γ-morpholino-*n*-propyl (75·2%), b.p. 147—149°/21 mm., and δ-morpholino-*n*-butyl alcohol (37·5%), b.p. 127—130°/2 mm. NH_2·CMe_2·CH_2·OH, Cl·$[CH_2]_2$·$]_2O$, and K_2CO_3 at 170° give *β-morpholinoisobutyl alcohol* (39·1%), m.p. 59—60° (uncorr.), b.p. 110—116°/2 mm; NH_2·CH_2·CHMe·OH gives similarly *β-morpholinoisopropyl alcohol* (42%), b.p. 82—84°/1·5 mm. γ-Morpholino-ββ-dimethylpropan-α-ol, b.p. 96—97°/2 mm., is obtained (82·6%) from the aldehyde. $Fe(NO_3)_3$,$9H_2O$, Na, and xylene are added successively to liquid NH_3 in CO_2–$COMe_2$–N_2; the NH_3 is removed; CH_2Ph·CN and then at 30—40° bromo*cyclo*hexane are added; after heating at 100°, 70% of phenyl*cyclo*hexylacetonitrile, m.p. 56—57°, is obtained; KOH–MeOH at 185—195° then gives the acid (92%), m.p. 152—153·5°. The following are prepared from the appropriate acid chloride and amine or alcohol in, usually, dioxan, $CHCl_3$, or C_6H_6. Unspecified m.p. in parentheses are those of *hydrochlorides*; antispasmodic activities relative to papaverine = 100 are also given. *β-Morpholinoethyl diphenylcarbamate*, m.p. 63·5—64·5° (m.p. 160—161°, 30), diphenylacetate (m.p. 137·5—138·5°, 75; *hydrobromide*, m.p. 119—120°, 40), benzilate (**I**) (from the acid in $Pr^{\beta}OH$) (m.p. 181·5—182·5°, 25), α-acetoxydiphenylacetate [from (**I**) and NaOAc in Ac_2O at 150—160°] (m.p. 186·5—187°, 25), α-chlorodiphenylacetate (m.p. 151·5—152·5°, 75); ββ-diphenylpropionate (m.p. 127—128°, 50), ββ′-diphenyl*iso*butyrate (m.p. 117—118°, 60), α-phenyl-α-*cyclo*hexylacetate (m.p. 147—148°, 100), triphenylacetate (+EtOH, m.p. 190·5—191·5°, 25), phenylacetate (+H_2O, m.p. 137—138°, 10), cinnamate (m.p. 216·5—217°, 40), *cyclo*hexanecarboxylate (+H_2O, m.p. 144—145°, 10—20), camphene-2-carboxylate (m.p. 202·5—203·5°, 60), trimethylacetate (*picrate*, m.p. 129·5—130·5°; 5), and ββ-dimethyl-*n*-butyrate (m.p. 152—153°; 5—10). *γ-Morpholino-ββ-dimethyl-n-propyl diphenylacetate*, m.p. 54·5—55·5° (m.p. 149·5—150°, 200; *sulphate*, m.p. 140—141°, 200), *α-phenyl-α-cyclohexylacetate*, m.p. 77° (m.p. 127·5—128·5°, 10), *benzoate*, m.p. 55·5—56° (m.p. 161·5—162·5°, 40), and cinnamate (m.p. 140—150°, 40). γ-Morpholino-*n*-propyl (m.p. 119·5—120°, 75; *benzylobromide*, m.p. 137—138°, 50), β-morpholino*iso*propyl (m.p. 214·5—215°, 60), δ-morpholino-*n*-butyl (m.p. 118—119°, 60), and β-morpholino*iso*butyl (m.p. 124·5—125·5°, 60) diphenylacetate. *Diphenyl*-, m.p. 140—141° (m.p. 189—190°, 20), α-chlorodiphenyl- (m.p. 139—140°,

50), and *α-phenyl-α-*cyclo*hexyl-*, m.p. 152—153° (m.p. 107·5—109°, 50), *-acet-β-morpholinoethylamide*. Br·$[CH_2]_6$·Br and $CHPh_2·CO_2K$ are heated in xylene at 170—180°; addition of morpholine to the cold product and boiling gives ζ-morpholino-*n*-hexyl diphenylacetate (m.p. 113—114°; 150). In general pharmacological activity in the series requires a disubstituted Ac containing ⩽1 Ph; branching or lengthening of the alkyl chain increases activity. M.p. are corr. R. S. C.

2-Phenyloxazole and *o*-substituted derivatives [thereof]. W. E. Cass (*J. Amer. Chem. Soc.*, 1942, **64**, 785—787).—Addition of Et_2 *o-nitrobenzylideneaminoacetal*, b.p. 143—146°/2 mm., to stirred conc. H_2SO_4 at 0—5° and addition of the solution to, and heating with, P_2O_5–H_2SO_4 at 180° gives 54·5% of 2-*o-nitrophenyloxazole* (**I**), m.p. 38—39° (*picrate*, m.p. 90—92°), oxidised by $KMnO_4$ or Br–H_2O to *o*-$NO_2·C_6H_4·CO·NH_2$ and hydrogenated (Raney Ni; abs. EtOH; 3 atm.; 97%) to 2-*o-aminophenyloxazole* (**II**), m.p. 32—33° [*picrate*, m.p. 154—155°; *Ac*, m.p. 104—105°, *Bz*, m.p. 149—150°, *p-NHAc·*$C_6H_4·SO_2$, m.p. 207—208°, and thence (12% HCl) *sulphanilyl* (**III**), m.p. 172·5—173·5°, derivatives]. Similar treatment of *o*-$NO_2·C_6H_4·CO·NH·CH_2·CH(OEt)_2$ gives only 6% of (**I**) and other methods give none. Treatment of the diazonium chloride from (**II**) with HPO_2 gives 2-*phenyloxazole*, b.p. 225—228° (*picrate*, m.p. 115—116°). The antistreptococcal activity of (**III**) is about equal to that of sulphadiazine; (**III**) is not toxic in doses of 5—20 mg. per 20 g. body wt. R. S. C.

Action of ammonia, ammonium carbonate, carbamide, and dicarbamhydrazide on saccharin and thiosaccharin. (Signa.) A. Mannessier-Mameli (*Gazzetta*, 1941, **71**, 3—18).—In aq. EtOH, NH_3 converts saccharin (**I**) into NH_4 saccharinate (**II**), and thiosaccharin (**III**) into NH_4 thiosaccharinate (**IV**), with, at the b.p., saccharinimine (**V**) (cf. Mannessier-Mameli, *ibid.*, 1940, **70**, 855), previously regarded (A., 1935, 763) as *ψ*-saccharinamine. NH_4 carbonate with (**I**) at 100° gives (**II**), and at 250°, (**V**); with (**III**) at 110° it gives (**IV**), and at 300°, (**V**), with some (**I**). With $CO(NH_2)_2$ (**VI**) in aq. EtOH, (**I**) is unchanged, or at the b.p. gives (**II**). At 150°, (**I**) and (**VI**) give *carbamide saccharinate*, $C_7H_5O_3NS,2CO(NH_2)_2$, m.p. 204° (decomp.), with a product (**VII**), m.p. 365—370°; at 250°, (**V**) and (**VII**) are formed. With (**VI**) in cold aq. EtOH, (**III**) gives a small amount of a *substance*, $C_{18}H_{16}O_5N_2S_3$ (**VIII**), m.p. 215°, which may be a mixture of *N*-ethyl-saccharin and -thiosaccharin; at the b.p., some (**V**) and a mixture, m.p. 175°, of (**I**) and (**III**) are formed. $(NH·CO·NH_2)_2$ with (**I**) in aq. EtOH is unchanged, or at the b.p. gives some (**II**); with (**III**), (**IV**), or at the b.p. (**VIII**) is formed. E. W. W

Action of hydrazine on saccharin and thiosaccharin. (Signa.) A. Mannessier-Mameli (*Gazzetta*, 1941, **71**, 18—25).—With N_2H_4 in aq. EtOH, saccharin gives hydrazine saccharinate, $C_7H_5O_3NS,N_2H_4$, m.p. 145° (resolidifying at 147°, decomp. ~175°), sweet; thiosaccharin gives *saccharin hydrazone*, m.p. 257—260° [regarded by Schrader (A., 1917, i, 709) as *ψ*-saccharinhydrazide], tasteless, also obtained by hydrolysing saccharin semicarbazone. E. W. W.

Action of semicarbazide on saccharin, thiosaccharin, and acetylsaccharin. (Signa.) A. Mannessier-Mameli (*Gazzetta*, 1941, **71**, 25—40).—Saccharin (**I**) and semicarbazide (**II**) in aq. EtOH give [with, on heating, $(NH·CO·NH_2)_2$ (**III**)] o-*sulphonamidobenzsemicarbazide* (**IV**), decomp. 210—215°, hydrolysed by NaOH, and converted by conc. HCl into (**I**), and by NH_2OH into (**I**) and some *saccharin semicarbazone* (**V**), m.p. 230—235° (decomp.) [*Na* salt, m.p. 293—295° (decomp.); Ac_3 derivative, m.p. 195—198°]. In aq. EtOH, (**II**) and thiosaccharin give (**V**), with, on heating, (**III**); (**II**) and *N*-acetylsaccharin give (**I**) and (**IV**). The new compounds are tasteless. E. W. W

Thiazoles, benzthiazoles, and benzselenazoles.—See B., 1942, II, 315, 318, 319, 348.

VII.—ALKALOIDS.

Aconite alkaloids. VIII. Atisine. IX. Isolation of two new alkaloids from *Aconitum heterophyllum*, heteratisine and hetisine. W. A. Jacobs and L. C. Craig. **X. Napelline.** L. C. Craig and W. A. Jacobs (*J. Biol. Chem.*, 1942, **143**, 589—603, 605—609, 611—616; cf. A., 1942, II, 40).—VIII. Data of Lawson *et al.* (A., 1937, II, 527) are in part corr. Atisine (**I**), $C_{22}H_{33}O_2N$, amorphous, m.p. 57—60° [hydrochloride, m.p. 311—312° (decomp.), $[\alpha]_D^{25}$ +28° in H_2O] (prep. from the roots of *A. heterophyllum*; 98 g. from 12 kg.), is unstable in EtOH and contains 2 OH, giving a *diacetate hydrochloride*, m.p. 241—243° (decomp.), but with MgMeI giving no CH_4 at 25° and 0·472 CH_4 at 95°. In NaOH–MeOH at 100° it gives, ? by disproportionation, ? *dihydroatisine* (**II**), m.p. 156—158° (corr.) [*hydrochloride*, m.p. 261—263° (decomp.), $[\alpha]_D^{27}$ −16° in H_2O], previously (*loc. cit.*) considered to be demethylated (**I**) and obtained with other substances by boiling KOEt–EtOH–N_2. Hydrogenation (PtO_2; MeOH; 3 atm.) of (**I**) gives mixed H_4-derivatives, including a *form*, m.p. 171—174°, $[\alpha]_D^{25}$ −33° in PhMe, −23° in $CHCl_3$, stable to alkali, also obtained in an attempted dihydrogenation (Pd-black; OH, 3 atm.) from (**I**). Na–EtOH converts (**I**) into a mixture whence only (**II**) was isolated. Kuhn–Roth determination shows ⩽1 NMe. With Se–N_2 at 340°, (**I**) gives *bases*, (*a*) ? $C_{21}H_{31}ON$, m.p. 180—190°, (*b*) $C_{16}H_{15}N$, tertiary, m.p. 83—85° (*picrate*, m.p. 221—223°; *methiodide*, m.p. 233—235°), (*c*) ? $C_{20}H_{29}N$ (*picrate*, m.p. 210—213°), and (*d*) ? $C_{20}H_{27}ON$ (*picrate*, m.p. indefinite), 1-methylphenanthrene, and hydrocarbons, (*a*) $C_{17}H_{16}$, m.p. 41—43° [*picrate*, m.p. 129—131°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 145—148°], and (*b*) $C_{18}H_{18}$ [*picrate*, m.p. 153—156°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 163—166°), both shown by absorption spectra to be phenanthrene derivatives. (**I**) is pentacyclic.

IX. The mother-liquors from (**I**) yield *heteratisine* (**III**), $C_{22}H_{33}O_5N$, m.p. 262—267° (decomp.), $[\alpha]_D^{27}$ +40° in MeOH [2 active H; *hydrochloride*, m.p. 265—270° (sintering and decomp. from >255°)], and *hetisine*, $C_{20}H_{27}O_3N$, sinters at >245°, m.p. 253—256°, $[\alpha]_D^{25}$ +13·7° in EtOH [*hydrochloride*, decomp. 300° (306—308°) after sintering; H_2-derivative *hydrochloride*, decomp. 333° after softening; 3 active H], stable to alkali. (**III**) contains a lactone ring, opened by NaOH which does not otherwise affect the mol.

X. Napelline (**IV**), $C_{22}H_{33}O_3N$, ? amorphous, m.p. 85—88°, contains 3 active H and 1 NMe, but no OMe. Hydrogenation (PtO_2; MeOH; 3 atm.) of its *hydrobromide*, m.p. variable, 227—230° (237—240°) after softening, gives *dihydronapelline*, m.p. (micro) 145—160° (clear at 165°) (*hydrobromide*, m.p. 256—258° after softening), and dehydrogenation (Se–N_2; 340°) gives an *alkyl-*, $C_{18}H_{18}$, m.p. 76—79° [*picrate*, m.p. 132—134°; *s*-$C_6H_3(NO_2)_3$ compound, m.p. 150—153°; structure proved by absorption spectrum], and dimethyl- (? ethyl)-phenanthrene (*picrate*, m.p. 142—146°; cf. Freudenberg *et al.*, A., 1938, II, 74, 179). R. S. C.

Argentine plants. III. Alkaloids from *Lycopodium saururus*. V. Deulofeu and J. De Langhe (*J. Amer. Chem. Soc.*, 1942, **64**, 968—969; cf. A., 1940, III, 832).—Leaves of *L. saururus* (7·4 kg., air-dry) yield to 2% HCl *tert.* bases, saururine, $C_{10}H_{19}N$, an oil [isolated as *picrate* (3·3 g.), m.p. 202°; *methiodide*, m.p. 242—244°], and *sauroxine* (0·5 g.), $C_{17}H_{26}ON_2$, m.p. 198° $[\alpha]_D^{20}$ −71·8° in EtOH (no OMe; *methiodide*, m.p. 258°]. R. S. C.

Cinchona alkaloids in pneumonia. X. *apo*Cupreine 6-*β*-alkylthiolethyl ethers. R. S. Tipson and L. H. Cretcher (*J. Amer. Chem. Soc.*, 1942, **64**, 1162—1164; cf. A., 1942, II, 381).—Prep. of *apo*cupreine, +1·5H_2O (lost at 140°/20 mm.) (H sulphate, $[\alpha]_D^{25}$ −223° in H_2O), its Cl·$[CH_2]_2$ ether (**I**), m.p. 168° (decomp.), $[\alpha]_D^{22}$ −179·5° in abs. EtOH (dihydrochloride), and *p*-$C_6H_4Me·SO_2·[CH_2]_2$·Cl, m.p. 22·5°, b.p. 140°/1·5 mm., is modified. With RSH and KOH in boiling abs. EtOH, (**I**) gives apo*cupreine β-methyl-*, m.p. 155°, [α] −175° in EtOH ([α] −220°; this and other [α] in parentheses are those of the *dihydrochlorides* in H_2O), *-ethyl-* (**II**), m.p. 144—145°, [α] −172° in EtOH ([α], +2H_2O, −198°), -n-*propyl-*, m.p. 147—148°, [α] −165° in EtOH ([α] −210° in H_2O, −176° in EtOH), -n-*butyl-*, *forms*, m.p. 141—142° and 120—121°, [α] −153° in EtOH ([α] −182°), *-phenyl-*, m.p. 150—151°, [α] −149° in EtOH ([α] −168° in EtOH), and *-benzyl-* (**III**), m.p. 101—102°, [α] −133° in EtOH, ([α] −162°), *-thiolethyl ether*. The *in vitro* effect against pneumococcus and the toxicity (mice) increase as R changes from Me to Bu and the SMe equals the SPh compound. Oral administration (mice) of (**II**) and (**III**) has no protective effect. The effect of (**I**) equals that of the Et ether. R. S. C.

***N*-Allylnormorphine.** J. Weijlard and A. E. Erickson (*J. Amer. Chem. Soc.*, 1942, **64**, 869—870).—Normorphine, m.p. (+0·5MeOH) 272—273° or (solvent-free) 276—277°, with CH_2:$CH·CH_2Br$ in $CHCl_3$ at 100° gives *N-allylnormorphine*, m.p. 208—209° (*hydrobromide*, m.p. 258—259°) (cf. McCawley *et al.*, A., 1941, II, 111), readily converted by $NPhMe_3·OH$ into allylnorcodeine. R. S. C.

Electrolytic reduction of strychnine. B. M. G. Zwicker and R. J. Robinson (*J. Amer. Chem. Soc.*, 1942, **64**, 790—793).—Electrolytic reduction of strychnine (**I**) at a Hg cathode in 60% H_2SO_4 gives rapidly good yields, according to the conditions (mainly temp.), of strychnidine or tetrahydrostrychnine, separated by the differing solubility in H_2O after removal of (**I**) as H sulphate from 28·5% H_2SO_4. Current efficiency is 16% at 27°, 2·4% at 6°, and very low at 66°. At a Na–Hg cathode reduction is still faster but gives dihydrostrychnidine (20—30%). At PbO_2, Cu, Ta, or Pt cathodes yields are very poor. R. S. C.

Alkaloids of American hellebore.—See A., 1942, III, 723.

VIII.—ORGANO-METALLIC COMPOUNDS.

Aliphatic arsinic acids. IV. Dichloroarsinoacetic acid. A. R. Marquez (*Rev. Fac. Cienc. Quím., La Plata*, 1941, **16**, 109—116).—$AsO_3H_2·CH_2·CO_2H$ with PCl_3 gives *dichloroarsinoacetic acid*, $AsCl_2·CH_2·CO_2H$, m.p. 112°, also obtained from (:As·$CH_2·CO_2H)_3$ with dry Cl_2 at 0°. F. R. G.

Diazonium borofluorides. III. Their use in the Bart reaction. A. W. Ruddy, E. B. Starkey, and W. H. Hartung (*J. Amer. Chem. Soc.*, 1942, **64**, 828—829; cf. A., 1937, II, 406).—Use of diazonium

borofluorides in the Bart reaction gives improved yields of $RAsO_3H_2$ (14 examples). R. S. C.

Preparation of phenylarsenoxides. V. Arsenoxides of naphthalene and diphenyl. G. O. Doak, H. Eagle, and H. G. Steinman (*J. Amer. Chem. Soc.*, 1942, **64**, 1064—1066; cf. A., 1941, II, 272).—*4-Nitro-1-naphthyl benzoate* (prep. by BzCl–NaOH), m.p. 176°, with H_2–Raney Ni in $COMe_2$ gives 4-amino-1-naphthyl benzoate hydrochloride, m.p. 258—262° (decomp.), which by the Scheller–Bart (not Bart) reaction gives 2·5% of *4-hydroxy-1-naphthylarsinic acid*, m.p. >360°. 6 : 2-$NH_2{\cdot}C_{10}H_6{\cdot}AsO_3H_2$ by the Sandmeyer reaction [$Ni(CN)_2$] and then hydrolysis gives *6-carboxy-2-naphthylarsinic acid* (22%), converted by PCl_3–PCl_5–$CHCl_3$ and then aq. NH_3 into *6-carbamyl-2-naphthylarsenoxide* (91%), amorphous. Monodiazotisation of benzidine and then treatment with $NaAsO_2$–$CuSO_4$ gives only (3·4%) *diphenyl-4 : 4′-diarsinic acid*. 4-$NH_2{\cdot}C_6H_3{\cdot}C_6H_4{\cdot}NO_2$-4′ gives (Scheller–Bart) *4-nitro-* (34%) and thence (H_2–Raney Ni) *4-amino-diphenyl-4′-arsinic acid* (80%) (*Ac* derivative), which, as above, yields *4-carbamyldiphenyl-4′-arsenoxide* (85%), m.p. 271—273°. By the Bart reaction 3-nitrobenzidine gives *3-nitro-4-aminodiphenyl-4′-arsinic* (**I**) (14·9%) and *3-nitrodiphenyl-4 : 4′-diarsinic acid* (19·4%), m.p. 249·5—250·5°. In boiling 25% KOH, (**I**) gives *3-nitro-4-hydroxydiphenyl-4′-arsinic acid* (75%). SO_2 reduces $RAsO_3H_2$ to *2-naphthyl-* (90%), *4-* (71%), m.p. 272°, and *2-acetamido-1-naphthyl-* (65%), m.p. 256·5°, and *4-aminodiphenyl-4′-* (100%), +$2H_2O$, m.p. 221—222° (*Ac* derivative, +H_2O, m.p. 297·5—298·5°), *-arsenoxide*. M.p. are corr. R. S. C.

Hexacovalent complexes of rhodous halides with diphenylmethylarsine.—See A., 1942, I, 337.

Substituted *p*-hydroxy-*m*-*N*-glycinylarsenobenzenes.—See B., 1942, II, 316.

Mercuri-alkylphenol derivatives.—See B., 1942, III, 204.

Relative reactivities of organo-metallic compounds. XLIV. Diazotisation of a lead aminoaryl compound. H. Gilman and C. G. Stuckwisch (*J. Amer. Chem. Soc.*, 1942, **64**, 1007—1008; cf. A., 1942, II, 183).—Successive addition of *p*-$C_6H_4Br{\cdot}NH_2$, $MgBr_2$–Et_2O, $PbPh_3Cl$, and aq. NH_4Cl to $LiBu^a$ in Et_2O at room temp. gives *Pb* Ph_3 p-*aminophenyl* (66%), m.p. 166—167°, which by diazotisation and coupling with β-$C_{10}H_7{\cdot}OH$ gives *Pb* Ph_3 p-2-*hydroxy-1-naphthylazophenyl* decomp. 135°, red in acid, green in alkali. R. S. C.

Organo-metallic compounds and their uses. G. N. Copley (*Ind. Chem.*, 1942, **14**, 201—205, 280—283).—A review.

IX.—PROTEINS.

Determination of the mol. wt. of degradation products of the proteins by precipitation-titration. B. Jirgensons (*J. pr. Chem.*, 1942, [ii], **159**, 303—312).—Degradation products of casein, deaminocasein, and gelatin can be determined by pptn.-titration using glycine, glycylglycine, and compounds of lower mol. wt. and non-degraded proteins as standard substances. As in other polymeric-homologous series, the precipitability has a linear relationship to the concn. of the degradation products. H. W.

Determination of the mol. wt. of degradation products of edestin by precipitation-titration. B. Jirgensons (*J. pr. Chem.*, 1942, [ii], **160**, 65—73).—Edestin is decomposed by 8M-$CO(NH_2)_2$ [4 hr. on bath (100°), 8 hr. reflux] (cf. Pauli *et al.*, A., 1935, 822), and the mean mol. wt. of the product is determined by pptn.-titration (3800—5300). Cryoscopic measurements indicate a mol. wt. of 6100. A. T. P.

Study of ovalbumin and its degradation products by precipitation-titration. B. Jirgensons (*Kolloid-Z.*, 1942, **98**, 70—75).—The relation $\gamma = a - \log c$, in which c denotes the concn. of an aq. solution of ovalbumin (**I**) and γ the concn. of $COMe_2$ needed to produce turbidity, is valid in the range 15—20° (cf. Schulz, A., 1937, **I**, 510). At higher temp. (40—45°) less $COMe_2$ is required for pptn. and the γ-c relation is less simple. The straight lines for different specimens of (**I**) are parallel and thus indicate a spherical shape for the (**I**) mol. A similar relation is found for lysalbic acid (**II**) and for a more degraded product (**III**) obtained by hydrolysis with NaOH, but not for a no. of physiological NH_2-acids. The mol. wts. of (**II**) and (**III**), calc. by the use of a similar formula, are 4400 and 470, respectively. F. L. U.

Viscosity and molecular decomposition of proteins. B. Jirgensons (*J. pr. Chem.*, 1940, [ii], **160**, 120—132).—Measurements of η observed during denaturing and decomp. of proteins by various agents (*e.g.*, warm aq. NaOH or HNO_2) show that in the case of proteins, *e.g.*, edestin, ovalbumin, and casein, the val. of η increases, reaches a max., and then falls, whereas with linear proteins, *e.g.*, gelatin, there is no increase, but only a lowering in the val. of η. In the former case, there is probably a loosening of the relatively compact protein to give long chain mols., whereas in the latter case, decomp. is accompanied by shortening of the chain. A. T. P.

***X*-Ray analysis of protein denaturation. II.** M. Spiegel-Adolf and G. C. Henny (*J. Physical Chem.*, 1942, **46**, 581—586; cf. A., 1941, II, 306).—Heat-denatured serum-pseudoglobulin (**I**) shows a characteristic sharpening of the backbone reflexion, but no additional rings as with serum-albumin (**II**). The *X*-ray change is irreversible and occurs even when coagulation is prevented. Thyroglobulin behaves similarly. Denaturation of (**I**) by EtOH produces the same change as does heat-denaturation. The diffraction pattern of dried (**I**) is not substantially changed by *X*-ray irradiation. Denaturation of (**II**) by adsorption at a PhMe interface does not lead to backbone sharpening, nor is this produced by subsequent heating. F. L. U.

Critical peptisation temperature of zein in concentrated ethyl alcohol.—See A., 1942, I, 327.

Tryptophan-containing acid hydrolysates of proteins suitable for intravenous administration.—See A., 1942, III, 757.

Isolation of *meso-* and *dl*-lanthionine from various alkali-treated proteins. M. J. Horn, D. B. Jones, and S. J. Ringel (*J. Biol. Chem.*, 1942, **144**, 87—91, 93—97; cf. A., 1941, II, 188).—*meso*-Lanthionine (**I**) is isolated from Na_2CO_3-treated human hair (2·5%), chicken feathers (0·25%), and lactalbumin (0·25%). 1%, 0·8%, or 0·1% of (**I**) is obtained from wool treated with boiling 0·1N-NaOH or 2% aq. Na_2S for 1 hr., or 2% aq. Na_2S at 37° for 6 days, respectively. (**I**) may probably be obtained similarly from most proteins which yield cystine on acid hydrolysis. In addition to (**I**), Na_2CO_3-treated human hair affords an equal amount of more sol. compound with similar properties to (**I**), which is most probably *dl*-lanthionine, decomp. 283—284° (Bz_2 derivative, new m.p. 195—198°). A. T. P.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Constituents of *Caucalis scabra*, Makino. I. Separation. II. Caucalol and *apo*caucalol diacetates. III. *iso*Cauealol and *apo*caucalol, saponification products of caucalol and *apo*caucalol diacetates. IV. Dehydrogenation of caucalol diacetate and *iso*caucalol. S. Mitsui (*Bull. Inst. Phys. Chem. Res. Japan*, 1941, **20**, 529—532, 533—539, 540—548, 549—555).—**I.** The C_6H_6 extracts of the seeds yields *caucalol diacetate* (**I**), $C_{19}H_{35}O_5$, m.p. 121—122°, $[\alpha]_D^{15.5}$ +33·4° in $CHCl_3$, and *apocaucalol diacetate* (**II**), $C_{19}H_{30}O_5$, m.p. 165°, $[\alpha]_D^{17.5}$ −126·4° in $CHCl_3$.

II. Both substances have 2 *tert.* OAc and 1 ether linking.

III. Saponification of (**I**) gives *isocaucalol* (**III**), $C_{15}H_{26}O_3$, m.p. 120—121°, $[\alpha]_D^{13.5}$ −99·1° in $CHCl_3$, which on re-acetylation gives *diacetates* of m.p. 58° and 86° and $[\alpha]_D^{25}$ −77·6° in $CHCl_3$. (**II**) is hydrolysed to *apocaucalol*, m.p. 139—140°, $[\alpha]_D^{21.5}$ −261·9° in $CHCl_3$.

IV. Dehydrogenation (Pd–C) of (**III**) or (**I**) yields an azulene derivative [$C_6H_3(NO_2)_3$ complex, m.p. 115—131°]. (**III**) with HI–red P, followed by dehydrogenation (Se), gives a $C_{10}H_8$ derivative [$C_6H_3(NO_2)_3$ complex, m.p. 165—168°] and, with Pd–Al_2O_3, a deoxy-derivative, m.p. 99—100°. F. O. H.

Chemical investigation of *Tinospora cordifolia* (Miers). B. V. Bhide, N. L. Phalnikar, and K. Paranjpe (*J. Univ. Bombay*, 1941, **10**, *Part* 3, 89—92).—The following have been isolated from the stems: *bitter principle* A, $C_{22}H_{31}O_{10}{,}3H_2O$, m.p. 226—228°, $[\alpha]_D^{26}$ +48° in $COMe_2$ (*acetate*, m.p. 213°), which does not contain OMe, OEt, CO, or CHO and cannot be methylated. It is hydrolysed by acids to a dark, amorphous material and the solution becomes fluorescent; phenyl-osazone or -hydrazone could not be obtained from the residue; *bitter principle* B, m.p. 186—188°, isolated in very small amount; a neutral substance, m.p. 82—83° (acetate m.p. 75°), probably octacosanol; a dark green oil which appears to contain glycerides of myristic and palmitic acid. H. W.

XI.—ANALYSIS.

Universal apparatus for micro- on semimicro-determination of carbon and hydrogen. G. Ingram (*J.S.C.I.*, 1942, **61**, 112—115).—The combustion apparatus described previously (A., 1939, II, 193) has been improved. The heating is now electrical and capable of very exact control; a new type of manometer which affords complete protection against loss of vapours in the event of an explosion is illustrated. A description is given of a special filling which absorbs quantitatively halogens, S, As, Sb, and Hg. 14 examples of typical results, using 3—20 mg. of substance, are given. Blumer's absorption tubes of different sizes are employed for collecting the products of micro- and semimicro-scale combustions, but the same combustion tube is retained throughout.

Semi-micro-determination of carbon using the Van Slyke–Folch oxidation mixture. R. M. McCready and W. Z. Hassid (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 525—526).—The sample is wet-oxidised with the Van Slyke–Folch reagent (CrO_3–H_2SO_4–SO_2–H_3PO_4+H_2O.)

and the CO_2 is absorbed on NaOH–asbestos and weighed. The method is successful with compounds which are incompletely oxidised by other wet-oxidation methods. The apparatus is described in detail. J. D. R.

Mercury azotometer for determination of organic nitrogen by the micro-Dumas method. R. G. Clarke and W. R. Winans (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 522—523).—The construction and operation are described of an azotometer, in which the N_2 produced by the Dumas method displaces Hg which is weighed. Accuracy is good. J. D. R.

Determination of fluorine and other halogens in organic compounds. P. J. Elving and W. B. Ligett (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 449—453).—The sample is heated with Na or K in a sealed tube at 400°. The solution in EtOH is neutralised (HNO_3); Cl, Br, and I are determined as the Ag salts, and F as PbClF. Apparatus is described and the technique for dealing with solids, liquids, and gases is detailed. J. D. R.

Determination of arsenic in organic compounds. Iodometric semi-micro-procedure. H. A. Slovites, W. M. McNabb, and E. C. Wagner (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 516—519).—The sample is decomposed by H_2SO_4–HNO_3, As pptd. with NaH_2PO_4, washed, and dissolved in excess of Br, and the excess titrated with $NaAsO_2$ buffered with Na_2HPO_4. The procedure is applicable in presence of halogens. J. D. R.

Electrometric titration of the carbonyl group. A. Eitel (*J. pr. Chem.*, 1942, [ii], **159**, 292—302).—The CO-compound (PhCHO, furfuraldehyde, $COMe_2$, MeCHO, *o*-C_6H_4Cl·CHO, *o*-NO_2·C_6H_4·CHO, *o*-OH·C_6H_4·CHO) is dissolved in EtOH if necessary and any acid neutralised with 0·1N-NaOH to phenolphthalein. The solution is treated with at least twice the requisite amount of NH_2OH,HCl or $(NH_2OH)_2,H_2SO_4$. After completion of oximation, the solution is diluted with H_2O, any sparingly sol. oxime is removed, and the filtrate is titrated with 0·1N-NaOH to p_H 4·1 using glass and normal HgCl electrodes. H. W.

Physical micro-methods for qualitative analysis of mixtures of organic substances. L. Kofler and M. Brandstätter (*Angew. Chem.*, 1942, **54**, 322—324).—The mixed m.p. is determined under the microscope; the component of lower m.p. is repeatedly removed with filter-paper, leaving a pure component. Examples are given, data tabulated, and procedure in presence of mol. compounds and mixed crystals is considered. A. A. E.

Conductometric titrations in non-aqueous solutions. J. T. Pinkston and H. T. Briscoe (*J. Physical Chem.*, 1942, **46**, 469—473).—Org. acids can be titrated conductometrically in NH_2·$[CH_2]_2$·OH. Complex ammine formation can also be followed. C. R. H.

Indicator method of classifying acids and bases in qualitative organic analysis. D. Davidson (*J. Chem. Educ.*, 1942, **19**, 221—226). L. S. T.

Titration of weak bases and strong acids.—See A., 1942, I, 338.

Investigation of amino-acid reactions by methods of non-aqueous titrimetry. I. Acetylation and formylation of amino-groups. J. J. Kolb and G. Teonnies. **II. Differential acetylation of hydroxy-groups, and a method for the preparation of *O*-acetyl derivatives of hydroxyamino-acids.** W. Sakami and G. Teonnies. **III. Determination of hydroxyl (and analogous) groups in amino-acids.** G. Teonnies and J. J. Kolb (*J. Biol. Chem.*, 1942, **144**, 193—201, 203—217; 219—227).—I. No large differences are noted in the rates of reaction between various NH_2-acids and Ac_2O or HCO_2H–Ac_2O in AcOH at room temp. Excess of free $HClO_4$ inhibits acylation. The course of *N*-acylation is followed by $HClO_4$ titration. During acetylation, and to a smaller extent during formylation, of cysteine, the $HClO_4$ titration val. passes through the normal min., but increases again. *N*-Acetyl-*dl*-alanine, -*dl*-methionine, -*l*-hydroxyproline, and -*dl*-tryptophan, *N*-formyl-*dl*-alanine and -*dl*-methionine, and *NN'*-diformyl-*l*-lysine, m.p. 132—133°, are prepared.

II. Reactions of hydroxy-amino-acids with Ac_2O–AcOH in presence of $HClO_4$ show that acetylation of NH_2 groups is increasingly suppressed by increasing acidity, whereas *O*-acetylation is promoted by $HClO_4$. The extent of the latter reaction can be determined by measuring the resulting decrease in Ac_2O available for reaction with NH_2-groups under basic conditions, the latter reaction being accompanied by loss of titratability of the NH_2 groups. Change from acid to basic conditions is effected by *o*-NH_2·C_6H_4·CO_2H addition, which also supplies excess of NH_2 groups. The hydroxy-amino-acid (1 mol.) is dissolved in conc. aq. $HClO_4$ (1·3 mols.)–AcOH and Ac_2O (1·4 mols.) is added carefully; after 1 hr. at room temp., H_2O is added and after a further hr., C_5H_{11}·NH_2 is added and the *O*-Ac-derivative pptd. by a suitable solvent, *e.g.*, EtOH, Et_2O, $COMe_2$, etc. Rapid hydrolysis of O-*acetyl*-l-*tyrosine*, decomp. 213—214°, and -l-*hydroxyproline*, decomp. 179—181°, occurs with aq. NaOH, but the rotation of the hydrolysed compound is almost identical with that of the parent compound; acid causes a much slower hydrolysis. O-*Acetyl*-dl-*serine*, decomp. 143—144° (evolution of gas), and -dl-*threonine*, decomp. 146—149° (evolution of gas), are prepared.

III. OH and analogous groups, *e.g.*, ·NH· of tryptophan, :NH and (less reliably) ·SH groups, are determined in dry NH_2-acids by a titrimetric method based on the acid-catalysed acetylation of these groups by Ac_2O. Under the conditions, cystine reduces $HClO_4$. Diphenylguanidine is a more suitable primary standard than glycine for $HClO_4$ titration. A. T. P.

Chromatography of aminodicarboxylic acids on alumina.—See A., 1942, II, 301.

Reaction of molybdenum. L. Rovira (*Rev. Fac. Cienc. Quím., La Plata*, 1941, **16**, 235—242).—Optimum conditions for the determination of NHPh·NH_2 with Na_2MoO_4 require a 5% solution of NHPh·NH_2 with an equal vol. of H_2O and twice the vol. of 7N-H_2SO_4, and heating for 30 min. at 100°. The reaction is inhibited by $Fe(CN)_6'''$, $Fe(CN)_6''''$, $Pb^{\cdot\cdot}$, and $Sn^{\cdot\cdot}$. The sensitivity is 5×10^{-4}. F. R. G.

Determination of *p*-toluidine in the presence of its isomerides. C. H. Benbrook and R. H. Kienle (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 427—428).—The sample of amine is diazotised and kept at 45° for 3 hr.; under these conditions, *o*- and *m*-C_6H_4Me·N_2Cl are completely decomposed, and the *p*-isomeride is almost unaffected. Measurement of the evolution of N_2 gives a measure of the *p*-content of the mixture. J. D. R.

Determination of 2-methyl-1 : 4-naphthaquinone. A. R. Menotti (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 418—420).—The quinone is treated with 2 : 4-$(NO_2)_2C_6H_3$·NH·NH_2 and alcoholic NH_3, and the blue-green colour is measured photo-colorimetrically. J. D. R.

Fission of phenolic ethers by pyridine hydrochloride. III. Attempted determination of methoxy-groups in phenolic ethers by pyridine hydrobromide. V. Prey (*Ber.*, 1942, **75**, [*B*], 445—446).—The ether is heated with a weighed quantity of C_5H_5N,HCl (**I**) at 220° for 3—4 hr. and unused (**I**) is titrated with 0·1N-alkali hydroxide in presence of phenolphthalein (**II**) or electrometrically. $PhOMe + 5C_5H_5N,HCl = PhOH + 4C_5H_5N,HCl + C_5H_5NMeCl$. Good results are obtained with mono- and poly-ethers. OEt can be determined under rather more drastic conditions. If CO_2H is present (**II**) must be replaced by litmus but the results are unsatisfactory. The method cannot be used for NO_2-ethers. H. W.

Performance of some distillation columns for the fractionation of terpenes. I. Pyridine and nicotinic acid. P. C. Tompkins and C. L. A. Schmidt (*J. Biol. Chem.*, 1942, **143**, 643—653).—Vals. of the diffusion current *i* and of the half-wave potential are given for C_5H_5N (**I**) and nicotinic acid (**II**) in both buffered and unbuffered solutions. In the latter (**I**) is probably reduced to piperidine. The polarograph is not recommended for analysis of (**I**) solutions; if it is used, the solution should contain Na or K phosphate at $\geq$0·1N. concn. in the p_H range 6—8. The *i* of (**II**) depends on p_H, buffer capacity, and (**II**) concn.; no information regarding the no. of H· or electrons involved in its reduction was obtained. The anion of (**II**) is not reducible. (**II**) waves are attributed to the catalytic reduction of H· with the undissociated (**II**) mol. acting as a mild catalyst F. L. U.

Determination of quinine by absorption spectrophotometry. J. Carol (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 524—529).—For concns. $\geq$1·5 mg. per 100 ml. transmittance at 340 mμ. shows only slight deviation from the Beer–Lambert law. Strychnine, atropine, NHPhAc, acetylsalicylic acid, camphor, phenolphthalein, caffeine, most blue, green, and red dyes, glycerol, EtOH, sugars, and the Fe'''–H_3PO_4 complex do not interfere. A. A. E.

[Determination of] nicotine [as] silicotungstates. L. N. Markwood (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 474—476).—Although the granular nicotine salt of $4H_2O,SiO_2,12WO_3,4H_2O$ filters more rapidly than the lamellar salt of $4H_2O,SiO_2,12WO_3,22H_2O$, high accuracy cannot be attained with the former owing to incomplete recovery. A. A. E.

Quantitative spectroscopic analysis of proteins. A. M. Buswell and R. C. Gore (*J. Physical Chem.*, 1942, **46**, 575—581).—Procedure for the quant. analysis of a protein, based on the determination of the extinction coeffs. for infra-red mol. or group frequencies characteristic of various NH_2-acids, is outlined. Data for salmine, proline, arginine, and guanidine are presented and discussed. F. L. U.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

NOVEMBER, 1942.

I.—ALIPHATIC.

M.p. of impure organic compounds. E. Allen (*J. Chem. Educ.*, 1942, **19**, 278—281).—A discussion of principles. L. S. T.

New methods of preparative organic chemistry. XVII. Dehydrogenation with sulphur, selenium, and platinum metals. P. A. Plattner (*Angew. Chem.*, 1942, **55**, 131—137, 154—158).—A review.

Detection of free radicals by the mass spectrometer. G. E. Eltenton (*J. Chem. Physics*, 1942, **10**, 403).—The detection of free radicals and intermediates in thermal decomp. reactions by a mass spectrometer is described. Me, but no CH_2, were detected from CH_4. CH_2 was detectable when a dil. mixture of diazomethane and He passed through the furnace. Production and removal of free radicals at temp. from 400° to 1000° and pressures 10^{-2} to 10 mm. have been studied by admixing 0·1% of $PbMe_4$ with C_2H_4, C_2H_6, and C_3H_6. Reaction with Me radicals is in the order $C_3H_6 > C_2H_6 > C_2H_4$. The vinyl radical could not be detected but the allyl radical was observed. CH_2O has also been detected. The possibility of applying the method at higher pressures is indicated. W. R. A.

Mild oxidation of long-chain hydrocarbons.—See B., 1942, II, 275.

Higher hydrocarbons. I. Seven alkyl-substituted docosanes. F. C. Whitmore, L. H. Sutherland, and J. N. Cosby (*J. Amer. Chem. Soc.*, 1942, **64**, 1360—1364).—*η*-, m.p. 3·2°, b.p. 194/1 mm., *ι*, m.p. 1·3°, b.p. 193°/1 mm., and *λ*-n-*butyl*-n-*docosane*, m.p. 0°, b.p. 194°/1 mm., are prepared, with special regard to purity, by the reactions, $RCO_2Me \rightarrow RCO_2H \rightarrow RCN \rightarrow (+MgBu^aBr)\ COBu^aR \rightarrow (MgR'Br)\ CBu^aRR'\cdot OH \rightarrow (CuSO_4;\ 175—180°)$ olefines $\rightarrow$ (Ni; 170°/1800 lb.) $CHBu^aRR'$. *ε*-n-*Butyl*-, m.p. 20·8°, b.p. 195°/1 mm., *η*-n-*hexyl*-, m.p. 19·3°, b.p. 209°/1 mm., *ι*-n-*octyl*-, m.p. 8·6°, b.p. 222°/1 mm., and *λ*-n-*decyl*-n-*docosane*, m.p. 1°, b.p. 235°/1 mm., are prepared by the reactions, $RCO_2Me + 2MgR'Br \rightarrow CRR'_2\cdot OH \rightarrow$ olefines $\rightarrow CHRR'_2$. *n*, *d*, and *η* are recorded. The following intermediates are described. Bu^aBr, b.p. 100°/740 mm., *n*-$C_6H_{13}Br$, b.p. 155°/738 mm., *n*-$C_8H_{17}Br$, b.p. 111°/47 mm., *n*-$C_{12}H_{25}Br$, b.p. 124°/20 mm.; Me *n*-dodecoate, b.p. 140°/15 mm., myristate, b.p. 140°/5 mm., palmitate, m.p. 29°, b.p. 163°/5 mm., and oleate, b.p. 175°/5 mm.; *n*-dodecoic, m.p. 44°, myristic, m.p. 54°, and palmitic acid, m.p. 63°; *n*-dodeco-, m.p. 4°, b.p. 160°/3 mm., myristo-, m.p. 19°, b.p. 168°/12 mm., and palmito-nitrile, m.p. 31°, b.p. 173°/17 mm.; *n*-hexadecan-, m.p. 36—37°, b.p. 145°/2 mm., *n*-octadecan-, m.p. 44—45°, b.p. 170°/2 mm., and *n*-eicosan-ε-one, m.p. 53—54°, b.p. 195°/2 mm. R. S. C.

α-Methylenic reactivity in olefinic and polyolefinic systems. E. H. Farmer (*Trans. Faraday Soc.*, 1942, **38**, 340—348).—Review and discussion of reactions involving the α-CH_2 of olefines and polyolefines, illustrated by reactions with $(CH\cdot CO)_2O$, org. peroxides, quinones, O_2, O_3, S, $Pb(OAc)_4$, SeO_2, and halogens, and by photogelation and thermal polymerisation. F. L. U.

Ionic and radical mechanisms in olefinic systems, with special reference to processes of double-bond displacement, vulcanisation, and photo-gelling. E. H. Farmer (*Trans. Faraday Soc.*, 1942, **38**, 356—361).—Possible ionic mechanisms in the displacement of double linkings in various olefinic systems under the influence of alkali are discussed. Such displacement in olefinic hydrocarbons and esters of vegetable oil acids, when caused by heat, is attributed to radical dissociation of α-CH_2 H atoms. The vulcanisation and photo-gelation of rubber are also attributable to radical mechanisms, since the most effective accelerators and sensitisers of these processes are substances that are prone to give free radicals as the result of thermal or photochemical decomp. F. L. U.

Course and mechanism of autoxidation reactions in olefinic and polyolefinic substances, including rubber. E. H. Farmer, G. F. Bloomfield, A. Sundralingam, and D. A. Sutton (*Trans. Faraday Soc.*, 1942, **38**, 348—356).—In unconjugated systems the primary reaction is entry of O_2 at α-positions to a double linking with formation of hydroperoxide groups, and not the bridging of a double linking by O_2. Conditions of formation and decay of hydroperoxide groups, electronic mechanisms, photo-peroxidation, and secondary reactions are discussed. F. L. U.

γη-**Dimethyl-**Δ^{β}-**octene.** S. Natelson, S. P. Gottfried, and S. Kornblau (*J. Amer. Chem. Soc.*, 1942, **64**, 1484—1485).—P_2O_5 converts citronellol or geraniol at 200—210° by dehydration and isomerisation into *γη-dimethyl-*Δ^{β}*-octene*, b.p. 162—163°/761 mm. (oxide, b.p. 179—183°, obtained by Bz_2O_2 in $CHCl_3$ at 0°) [and a small forerun (**I**), b.p. 159—162°], converted by O_3 into *Me isohexyl ketone* (**II**), b.p. 168—171° (*semicarbazone*, m.p. 146—147°). O_3 converts (**I**) into (**II**) and a fraction of higher b.p. R. S. C.

Systematics of mixed polymerisates.—See A., 1942, I, 370.

Quantitative oxidative fission of ozonides of olefines of high mol. wt. F. Asinger (*Ber.*, 1942, **75**, [*B*], 656—660).—Fission of the ozonides occurs readily and nearly quantitatively when they are added gradually to an alkaline suspension of Ag_2O at 90—95° and the mixture is kept at this temp. for some hr. Addition of dil. HNO_3 in slight excess ppts. the fatty acid. In this manner Δ^{α}-dodecene, Δ^{α}-tridecene, and other olefines give the corresponding acids in 95—98% yield. Possibly aldehydes are formed as intermediates since hept-, undec-, tetradec-, and hexadec-aldehyde are thus readily oxidised. There is no evidence of wandering of the double linking during fission of the ozonides with Ag_2O. The products of the fission invariably contain ~5% of neutral, non-olefinic substances with marked peroxide reaction; the yield appears to depend on the solvent used for ozonisation. H. W.

Methods of substituting alcoholic hydroxyl groups by bromine. [Preparation of alkyl bromides.]—See B., 1942, II, 273.

Pyrogenic syntheses of hydrocarbons in the " hot–cold " tube. II. R. Schwarz and D. Pflugmacher (*J. pr. Chem.*, 1941, [ii], **158**, 2—7).—Passage of CCl_4 in H_2 over a silite rod at 600—650° (contact for 10—30 sec.) gives Cl_2, HCl, C_6Cl_6 (60%), C_2Cl_4 (35%), C_2Cl_6 (5%), $CMeCl_3$ (0·01%), and $SiCl_4$. The reaction mechanism involves progressive loss of Cl and formation of radicals. R. S. C.

Composition of the products of halogenation of hydrocarbons of higher mol. wt. F. Asinger (*Ber.*, 1942, **75**, [*B*], 668—675).—Do-(**I**) and hexa-decane are chlorinated to ~50% reaction to avoid undue formation of di- and poly-chlorides and the monochlorides are isolated from the mixture by use of a Raschig column with high reflux ratio. These are dechlorinated by Ag stearate and the mixture is ozonised. The ozonides are oxidatively degraded by Ag_2O in alkaline suspension to the acids, which are separated by distillation into mixtures of $\geq$ two acids; the acid val. of each fraction is determined. Equimol. mixtures of all theoretically possible isomeric monochlorides are produced, the substituent being uniformly distributed over all CH_2 groups. Substitution in terminal Me is < in CH_2, the relative reactivities of primarily and secondarily united H being 1 : 3·25. Similar results are obtained by the bromination of (**I**). The distribution of the isomerides is not appreciably affected by use of various catalysts or temp. (100°, 200°, 300°). It is probable that similar relationships persist in other reactions and that, *e.g.*, by oxidation all theoretically possible acids are produced. The predominance of acids of lower mol. wt. in the resulting mixtures is due to after-oxidation of the more complex acids. H. W.

Elimination of hydrogen halide from alkyl halides of higher mol. wt. without displacement of the double linking. F. Asinger (*Ber.*, 1942, **75**, [*B*], 660—663).—Elimination of HHal occurs with relatively good yields when the alkyl halide is heated with Ag stearate or palmitate in C_6H_6 at 200—250° in a Pb- or Ag-lined autoclave; a stearate is formed intermediately. With *sec.*-alkyl halides a temp. of 200° suffices. Thus *η*-chloropentadecane gives Δ^{ζ}- and Δ^{η}-decene, *β*-chlorododecane yields Δ^{α}- (**I**) and Δ^{β}-dodecene, and *n*-dodecyl bromide affords (**I**). Elimination of primarily-united Cl is invariably accompanied by a slight displacement of the double linking such as is observed in the Grignard reaction. Such displacement is not observed with *sec.* halides. H. W.

tert.-**Amyl fluoride, b.p. 38°/458 mm.**—See A., 1942, I, 353.

Regularities in the elimination of hydrogen halide from alkyl halides of higher mol. wt. F. Asinger (*Ber.*, 1942, **75**, [*B*], 664—668).—Treatment of *η*-chloropentadecane with Ag stearate, ozonisation of the product, and oxidative fission of the ozonide with Ag_2O gives hexoic, heptoic, octoic, and nonoic acid and shows that elimination of HCl occurs in both possible directions. Similar dechlorination of *β*-chlorododecane gives 31 mol.-% of undecoic and 69 mol.-% of

decoic acid, showing that H is removed more readily from CH_2 than from CH_3. H. W.

Polyvinyl compounds. I. Reactions of polyvinyl chloride. V. V. Korschak and V. A. Zamiatina (*J. Appl. Chem. Russ.*, 1941, **14**, 809—815).—Polyvinyl chloride (I) is stable towards aq. alkalis at 100° (alone or in the presence of U oxide, Fe_2O_3 hydrate, Cu powder, or stearic or oleic acid), and also when autoclaved at 120°. The stability of (I) under these conditions is ascribed to its insolubility in aq. solutions. Treatment of solutions of (I) in $COMe_2$ by 50% KOH or NaOEt–EtOH (II) produces dark brown powders (III), insol. in H_2O and in org. solvents. Treatment of dioxan solutions of (I) with solid KOH, KOH–EtOH, or with (II) gives brown insol. powders (IV), in which some of the Cl has been substituted by OH and some has been eliminated with the formation of double linkings. Acetylation of (IV) with Ac_2O gives a dark-coloured insol. acetate, such as is obtained on acetylating a thoroughly dried polyvinyl alcohol. It is suggested that the insolubility of the products of hydrolysis of (IV) by alkalis is due to the formation of ethereal cross-linkings between separate macromol. chains during the elimination of Cl. Both (III) and (IV) become light yellow or colourless on keeping. The chromophoric groups responsible for the colour of (III) and (IV) are suggested to be the systems of conjugated and accumulated double linkings along the macromol. chains. The loss of colour on keeping may be due either to oxidation or to further polymerisation, as the Br nos. of (III) and (IV) fell on keeping. Zn powder acting on a dioxan solution of (I) does not eliminate as much of its Cl as has been found by Marvel (A., 1940, II, 62). The resulting product, $C_{13}H_{18}O_2Cl_3$, is white (Br no. nil). Na had hardly any action on (I) dissolved in carefully purified anhyd. dioxan, but removes up to 15% of its Cl when dissolved in the impure solvent, which contained $(CH_2{\cdot}OH)_2$ and H_2O; these gave rise to NaOH and Na alkoxide, with a consequent elimination of Cl. The non-interaction between (I) and Na, its weak interaction with Zn powder, and the absence of $(CH_2{\cdot}CO_2H)_2$ after oxidation with 20% HNO_3, lead to the conclusion that (I) is an $\alpha\gamma$-Cl_2-product. Oxidation of (V) by 20% HNO_3 produces $H_2C_2O_4$ and a monocarboxylic acid (mol. wt. 150) containing ~43% Cl; this points to an irregular distribution of double linkings, OH groups, and residual Cl in (V). N. G.

Manufacture of αα-dichloro-α-nitroparaffins.—See B., 1942, II, 274.

Hepene hydrochloride, $C_{45}H_{76}$,8HCl, m.p. 127°, and decabromide.—See A., 1942, III, 755.

Non-alkaloidal constituents of *Mandragora* root. H. Staub (*Helv. Chim. Acta*, 1942, **25**, 649—683).—The root of *M. autumnalis*, Spr., yields to light petroleum 0·6% of oil, containing sitosterol *d*-glucoside, m.p. 288—292° (decomp. from ~240°), melissyl cerotate, *n*-$C_{18}H_{32}$·, -$C_{17}H_{36}$, and -$C_{31}H_{64}$, m.p. 68·5°, f.p. 67°, *n*-$C_{22}H_{45}$·OH and -$C_{31}H_{63}$·OH, an alcohol [?] ($C_{31}H_{63}$·OH), m.p. 75·5—76°, a sterol, $C_{29}H_{50}O$, +H_2O, m.p. 128—129°, β-sitosterol (isolated by way of the acetate), and tripalmitin; hydrolysis yields cerotic, myristic, arachidic, behenic, stearic, palmitic (main unsaturated acid), lauric, (?) adipic, β-linoleic (53·6—82% of total acids), and β-linolenic acid, and *n*-tridecyl ketone. Subsequent extraction of the root with Et_2O–$CHCl_3$ and treatment with aq. NH_3 etc. yields *l*-tropic acid, m.p. 126·5—127·5°, $[\alpha]_D^{20}$ −70·11° in abs. alcohol, chrysatropic acid, sitosterol *d*-glucoside, and fats yielding sitosterol, an alcohol, m.p. 82—83°, a *diol*, $C_{22}H_{46}O_2$ or $C_{24}H_{50}O_2$, m.p. 101·5—102° (*diacetate*, m.p. 65·5°), and β-sitosterol. Final extraction with EtOH yields hyoscyamine, sitosterol *d*-glucoside, chrysatropic acid, glucose, and substances, m.p. 285—286° (decomp.), and decomp. 170—172°. Scopolin and tannins are absent. R. S. C.

Use of xanthates in identification of alcohols. I. S. Shupe (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 495—498).—M.p. and I equivs. are given for K xanthates of alcohols used in the prep. of cosmetics. M.p. of *K xanthates* are: $CH_2Ph{\cdot}OH$ 178—180°, diethylene glycol 207—208°, triethylene glycol 203—205°, $OH{\cdot}[CH_2]_2{\cdot}OPh$ 177—178°, $N([CH_2]_2{\cdot}OH)_3$ 212—214°. A. A. E.

Esters of arsenious acid. A. Dupire (*Compt. rend.*, 1942, **214**, 82—84).—*Arsenious esters* of the following have the b.p. given: β-ethylhexanol, 215°/8 mm., dodecan-α-ol, 300°/15 mm., Δ⁴-octadecen-α-ol, 305°/8 mm., $Ac{\cdot}[CH_2]_2{\cdot}OH$, 145°/6 mm., 2-methyl*cyclo*hexanol, 208°/6 mm., Et, 165°/5 mm., and Bu lactate, 235°/6 mm., propane-αβ-diol, 190°/16 mm., butane-αγ-diol, 215°/15 mm., α-chloropropane-βγ-diol, 220°/25 mm., γ-ethylidene-, 190°/15 mm., and γ-*cyclo*hexylidene-propane-αβ-diol, 350°/12 mm., and *o*-, 262°/15 mm., *m*-, 280°/22 mm., and *p*-cresol, 250°/5 mm. The rate of esterification is max. for C_7-primary alcohols and for di-primary alcohols. Phenols and *sec.* or halogenated alcohols esterify with difficulty. A. Li.

Manufacture of dihydric alcohols.—See B., 1942, II, 275.

***l*-Glycidol.** J. C. Sowden and H. O. L. Fischer (*J. Amer. Chem. Soc.*, 1942, **64**, 1291—1293).—*d*(+)-*iso*Propylideneglycerol (I) with *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N at room temp. and then 0·5N-HCl at 75—80° gives *l*-glyceryl α-*p*-toluenesulphonate, m.p. (crude) 60—61°, $[\alpha]_D$ −7·3° in C_5H_5N, which with NaOMe–MeOH–Et_2O at 6° gives *l*-glycidol (II), b.p. 56—56·5°/11 mm., $[\alpha]_D$ +15° (lit. +7·69°) (homogeneous) (p-*nitrobenzoate*, m.p. 59—60°, $[\alpha]_D^{20}$ +37·9° in $CHCl_3$). *dl-Glycidol* p-*nitrobenzoate*, m.p. 56°, and *dl*-glycerol α-*p*-nitrobenzoate, m.p. 106—107°, are prepared. The α-*p*-toluenesulphonate of (I) with anhyd. NH_3 at room temp. gives 1-β*γ*-iso*propylidenedioxypropylamine* (55%), b.p. 54—55°/8 mm., $[\alpha]_D$ +14·4° (homogeneous), −35·4° → −21·1° in 450 min. in HCl (excess), hydrolysed by boiling 0·1N-H_2SO_4 to *l*-βγ-dihydroxypropylamine, m.p. 55—57°, b.p. 95—98°/0·003 mm., $[\alpha]_D$ −28·4° (lit. −14·08°) in 5N-HCl, −2·4° (lit. −1·34°) in H_2O, also obtained ($[\alpha]_D$ −29·2°, −2·5°, respectively) from (II) by 28% aq. NH_3 at 0°. R. S. C.

Preparation of divinyl ether.—See B., 1942, II, 276.

Mechanism of the conversion of β-glycerophosphoric acid into the α-form. E. Chargaff (*J. Biol. Chem.*, 1942, **144**, 455—458).—β-Glycerophosphoric acid (I) is converted into the α-form in presence of H_2SO_4 and radioactive Na_2PO_4 (II) without an exchange between the phosphoric ester and the inorg. phosphate. Hydrolysis of (I) by kidney phosphatase in presence of (II) also occurs without labilisation of the phosphoric ester linking. A. T. P.

Qualitative study of some reactions of organic sulphides and especially those of ββ-dichlorodiethyl sulphide. I. Ribas, A. Caño, and A. S. Contra (*Anal. Fis. Quim.*, 1941, **37**, 478—486).—1 part in 200,000 of $S([CH_2]_2{\cdot}Cl)_2$ (I) in H_2O with a 1% aq. solution of phosphotungstic acid and 0·1% $AuCl_3$ gives a fluorescence. With higher concns. of (I) a ppt. is obtained. The reaction is not given by Et_2S, SCl_2, $AsCl_3$, $COCl_2$, $AsCl_2{\cdot}CH{:}CHCl$, $AsCl(CH{:}CHCl)_2$, diphenylaminochloroarsine, $CCl_3{\cdot}NO_2$, CH_2BzCl, $S(CH{:}CH_2)_2$, $S(CHMeCl)_2$, and org. solvents. The structure of the complex produced is considered. F. R. G.

Ammonolysis of esters. W. V. Sessions (*J. Chem. Educ.*, 1942, **19**, 130).—Me esters are the most reactive; with conc. aq. NH_3 at room temp. activity increases with an increase in mol. wt. of the alcohol or acid. Esters of *iso*-acids or -alcohols are less active than the *n*-compounds; all formates react readily. NaOMe is the best catalyst for the reaction between aq. NH_3 and BuOAc or *iso*-$C_5H_{11}{\cdot}OAc$. L. S. T.

Degradation of the salts of aliphatic acids by bromine. H. Hunsdiecker and C. Hunsdiecker (*Ber.*, 1942, **75**, [*B*], 291—297).—Reaction of the Ag salts of saturated fatty acids or of the Ag salts of H esters with Br gives 65—80% yields of Br-compounds. A small proportion of the bromide reacts with unchanged Ag salt to give an ester and some substitution of H by Br cannot be avoided. The Ag_2 salts of dicarboxylic acids give dibromides in 40—65% yield which can sometimes be increased by keeping Br in excess. Hg salts generally give equally good yields which may be diminished owing to decomp. of the Hg halides in the org. solvent during distillation; the change is greatly accelerated by light. K salts react relatively slowly with Br so that ester formation and substitution can scarcely be avoided. Qualitatively "salt degradation" by Cl_2 is similar to that by Br. The following *acids* and their *Me* esters (consts. in parentheses) are obtained: *δ-bromovaleric*, m.p. 39° (b.p. 101°/14 mm.); *ζ-bromoheptoic*, m.p. 30° (b.p. 112°/5 mm.); *η-bromo-octoic*, m.p. 37° (b.p. 124°/6 mm.); *θ-bromononoic*, m.p. 34° (b.p. 131°/2 mm.); *ι-bromodecoic*, m.p. 43° (b.p. 163°/12 mm.); *κ-bromoundecoic*, m.p. 50° (b.p. 176°/14 mm., m.p. 17°); *λ-bromododecoic*, m.p. 53° (b.p. 130°/0·05 mm., m.p. 7°); *μ-bromotridecoic*, m.p. 58° (b.p. 168°/2 mm., m.p. 30°); *ν-bromotetradecoic*, m.p. 63° (b.p. 168°/0·8 mm., m.p. 22°); *ξ-bromopentadecoic*, m.p. 66° (b.p. 186°/2 mm., m.p. 40°); *o-bromohexadecoic*, m.p. 71° (b.p. 210°/4 mm., m.p. 31°); *π-bromoheptadecoic*, m.p. 74° (b.p. 212°/2·5 mm., m.p. 48·5°). *δ-Iodovaleric*, m.p. 56°, *ζ-bromoheptoic*, m.p. 48°, *η-iodo-octoic*, m.p. 43·5°, *θ-iodononoic* m.p. 56°, *ι-iododecoic*, m.p. 53°, *κ-iodoundecoic*, m.p. 66°, *λ-iododododecoic*, m.p. 62·5°, *μ-iodotridecoic*, m.p. 71°, *ν-iodotetradecoic*, m.p. 71°, *ξ-iodopentadecoic*, m.p. 77°, *o-iodohexadecoic*, m.p. 75·5°, and *π-iodoheptadecoic*, m.p. 82°, *acid* are obtained from the Br-acids and NaI in $COMe_2$. The conversion of Hg and K octoate into α-bromoheptane is described. H. W.

Synthesis of free formic acid from carbon monoxide and water.—See B., 1942, II, 273.

Synthesis of acetyl fluoride and its derivatives. I. A. I. Maschentzev (*J. Appl. Chem. Russ.*, 1941, **14**, 816—826).—AcCl is added dropwise at room temp. to a stirred mixture of Ac_2O and the normal or H fluorides of K, Na, or NH_4, the temp. of the mixture gradually raised to 90—95°, kept at this temp. for 2—3 hr., and then for 1 hr. at 120—140°. The best yield (81—82%) is obtained with KHF_2. AcF is also prepared by gradually heating mixtures of Ac_2O and KHF_2, $NaHF_2$, NH_4HF_2, or KF to 160° and keeping the mixture at this temp. for 2½ hr. The best yields of AcF are obtained with KHF_2 (92%) and KF (83%). Data are given for the solubilities of the normal and H fluorides of K, Na, and NH_4 in AcOH at 16° and in Ac_2O at 16° and 25°. The mechanism of the above reactions is discussed. N. G.

Hydrogen fluoride as a condensing agent. XVI. Reactions of carbon monoxide. J. H. Simons and A. C. Werner (*J. Amer. Chem.*

Soc., 1942, **64**, 1356—1357; cf. A., 1941, II, 288).—Pr$^{\alpha}$OH and HF in 90% HCO_2H at 100—160° give 28% of Pr$^{\beta}CO_2H$, and *n*-C_5H_{11}·OH gives 11% of a C_6-acid, but Pr$^{\beta}$OH gives a neutral tar. Pr$^{\beta}$Cl with HF–Ni(CO)$_4$ at 150° (not 109°), HF–H_2O or –MeOH at 150°, or anhyd. HF at 160° gives 20, 56, 7, and 6%, respectively, of Pr$^{\beta}CO_2H$. Bu$^{\gamma}$Cl and HF–H_2O give only a trace of acid. The reaction mechanism is discussed. R. S. C.

Manufacture of salts of alkylacrylic acids.—See B., 1942, II, 276.

Heptoic acid and heptyl alcohol from heptaldehyde. L. J. Briusova and E. A. Ogorodnikova (*J. Appl. Chem. Russ.*, 1941, **14**, 636—639).—Heptaldehyde with a 1—1·25% solution of Al in heptyl alcohol at 26—30° affords a 94% yield of heptyl heptoate. G. A. R. K.

***cyclo*Pentane series. II. Experiments towards the synthesis of Wieland's C_{13} acid in proper stereochemical forms.** P. C. Dutta (*J. Indian Chem. Soc.*, 1942, **19**, 79—86; cf. A., 1942, I, 53).—CHNaAc·CO_2Et and Pr$^{\beta}$·$[CH_2]_3$·CHMeI (**I**) give *Et* αε-*dimethylhexylacetoacetate*, b.p. 122°/4 mm., converted by K in xylene followed by I·$[CH_2]_2$·OEt (**II**) into *Et* β-*ethoxyethyl*-αε-*dimethylhexylacetoacetate*, b.p. 138—142°/3·5 mm. (small yield). CHNa$(CO_2Et)_2$ and (**I**) afford *Et* αε-*dimethylhexylmalonate*, b.p. 128°/4 mm., and thence [K; (**II**)] *Et* β-*ethoxyethyl*-αε-*dimethylhexylmalonate* (**III**), b.p. 154—158°/5 mm. (**III**) is hydrolysed (EtOH–KOEt), the product decarboxylated, and then treated with $SOCl_2$–C_5H_5N to give α-α′ε′-*dimethylhexyl*-γ-*butyrolactone*, b.p. 125°/4 mm. CN·CHNa·CO_2Et and (**I**) afford *Et* αε-*dimethylhexylcyanoacetate*, b.p. 125°/5 mm., and thence *Et* β-*ethoxyethyl*-αε-*dimethylhexylcyanoacetate* (**IV**), b.p. 165°/7 mm. (**IV**) is hydrolysed (KOH–MeOH) and decarboxylated to β-*ethoxyethyl*-αε-*dimethylhexylacetonitrile*, b.p. 127°/5 mm., which with MeMgI in C_6H_6 gives α-*ethoxy*-γ-*acetyl*-δθ-*dimethylnonane* (**V**), b.p. 118°/4 mm. (**V**) is reduced (Na–*iso*-C_5H_{11}·OH) to the *OEtcarbinol*, b.p. 126—130°/4 mm., the *chloride* (**VI**), b.p. 122—124°/5 mm. (prep. by $SOCl_2$–C_5H_5N), from which with Hg$(CN)_2$ at 160—170° affords α-*ethoxy*-δθ-*dimethyl*-γ-*ethylidenenonane*, b.p. 94°/5 mm., also obtained from (**VI**) with NaI in EtOH. (**VI**) with MeMgI and CO_2 affords αγη-trimethyl-β-β′-ethoxyethylnonoic acid (with EtOH–H_2SO_4 gives the *Et ester*, b.p. 150—155°/7 mm., with or without the lactone formed by de-ethoxylation). C. S.

Long-chain acids containing a quaternary carbon atom. I. A. J. Birch and (Sir) R. Robinson (*J.C.S.*, 1942, 488—497).—An account of previous work on phthioic acid is given. αα-Dimethyl-lauric acid (**I**) has m.p. 4° (lit. val. 27° is for an impure specimen). Stearoylbenzene, $NaNH_2$, and PhMe refluxed for ½ hr. and, after adding MeI, for 2 hr. give an amide, m.p. 81°, which with H_2SO_4–$NaNO_2$ yields αα-*dimethylstearic acid*, m.p. 42°. α-*n*-Decyl-lauryl chloride with C_6H_6 ($AlCl_3$) yields ωω-*di*-n-*decylacetophenone*, b.p. 275—280°, which could not be methylated. *n*-$C_{10}H_{21}$·CN and *n*-C_8H_{17}Br ($NaNH_2$) afford α-n-*octylundeconitrile*, b.p. 215—220°/12 mm., hydrolysed (H_2SO_4–AcOH–H_2O or H_3PO_4 at 160°) to the *amide*, m.p. 109°. EtCN with *n*-$C_{10}H_{21}$Br gives α-*methyl*-α-n-*decyllauronitrile*, b.p. 230—245°/1 mm., resistant to hydrolysis. *n*-$C_{10}H_{21}$·CMe_2Cl with veratrole (CS_2, $AlCl_3$) yields 4-(αα-*dimethylundecyl*)*veratrole*, b.p. 220—225°/13 mm., demethylated (HBr) and then oxidised ($KMnO_4$) to (**I**). CO_2Et·CH_2·CMe_2·CH_2·COCl (**II**) and *n*-C_5H_{11}·CAcNa·CO_2Et afford a *product*, b.p. 200°/10 mm., which gives δ-*keto*-ββ-*dimethylundecoic acid*, b.p. 190°/10 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 122°), by successive treatment with 5% aq. NaOH, 5% aq. H_2SO_4, and 10% aq. NaOH. Similarly (**II**) and *n*-C_8H_{17}·CAcNa·CO_2Et afford a product converted into δ-keto-ββ-dimethyltetradecoic acid (2 : 4-dinitrophenylhydrazone, m.p. 85°; Et ester, b.p. 186—188°/9 mm.), reduced (Clemmensen) to ββ-*dimethyltetradecoic acid*, m.p. 15°. β-*Methyl*-β-n-*hexylglutaric acid*, m.p. 61° (prep. described), is converted into its chloride and this with CPrAcNa·CO_2Et yields a product, converted into a mixture of acids resolved by fractional distillation of the Me esters, giving *Me* δ-*keto*-β-*methyl*-β-n-*hexylnonoate*, b.p. 178—182°/10 mm. COMe·C_8H_{17}-*n*, CN·CH_2·CO_2Et (**III**), and saturated NH_3–EtOH give αα′-*dicyano*-β-*methyl*-β-*octylglutarimide*, m.p. 139°, which when refluxed with 50% H_2SO_4 affords β-methyl-β-*n*-octylglutarimide, m.p. 91°, hydrolysed (H_2SO_4–AcOH–H_2O) to the acid, the ester chloride of which with *n*-C_5H_{11}·CAcNa·CO_2Et yields a product converted into a mixture of acids containing δ-*keto*-β-*methyl*-β-n-*octylundecoic acid*, b.p. 235—240°/10 mm., reduced (Clemmensen) to β-methyl-β-*n*-octylundecoic acid, b.p. 225—230°/20 mm.

COMe·$C_{10}H_{21}$-*n*, (**III**), and NH_3–EtOH yield αα′-*dicyano*-β-*methyl*-β-n-*decylglutarimide*, m.p. 135°, converted into methyl-*n*-decylglutaric acid, m.p. 63—64° (anhydride, m.p. 31°; imide, m.p. 71°). α-Methyl-α-*n*-decylsuccinic acid yields an *anhydride*, m.p. 37° (by heating with Ac_2O), and an *imide*, m.p. 98° (by treating the ester chloride successively with aq. NH_3, aq. NaOH, and HCl). C_7H_{15}·MgBr (**IV**) and CO_2Et·CH_2·$CMe(C_8H_{17}$-*n*)·CH_2·COCl yield a product hydrolysed to δ-keto-β-methyl-*n*-octyl-lauric acid (*Me* ester, b.p. 235°/19 mm.). (**IV**) and ββ-dimethylglutaromethylimide give a product hydrolysed to δ-keto-ββ-dimethyl-lauric acid, b.p. 203°/18 mm. (semicarbazone, m.p. 113°; 2 : 4-*dinitrophenylhydrazone*, m.p. 99°). cyclo*Hexane*-1 : 1-*diacetomethylimide*, m.p. 66° (by distillation of its NH_3Me salt), and (**IV**) give a product hydrolysed to a mixture from which 1-β-*ketononyl*cyclo*hexane*-1-*acetic acid*, m.p. 151°, is obtained by fractionation of the esters. Raney Ni at 200°/50—60 atm. in EtOH reduces CH_2Bz·$CMe(C_6H_{13}$-*n*)·CH_2·CO_2Et to an *ester*, b.p. 190—200°/14 mm., hydrolysed to β-(β-*cyclo*hexylethyl)-β-methylnonoic acid, b.p. 225—228°/13 mm. α-*Phenacyl*-α-*methyl*-*lauric acid* (**V**), m.p. 87° (from α-methyl-α-*n*-decylsuccinic acid and C_6H_6), is similarly reduced to α-(β-*cyclo*hexylethyl)-α-methyl-lauric acid (*Et* ester, b.p. 245—250°/14 mm.). Reduction (Clemmensen) of (**V**) gives a mixture from which isomeric γ-*phenyl*-α-*methyl*-α-n-*decylbutyrolactones*, m.p. 102° and 164°, are isolated. α-Methyl-α-*n*-hexylsuccinic anhydride in C_6H_6 with $AlCl_3$ yields α-*phenacyl*-α-*methyloctoic acid*, m.p. 95°. Self-condensation of COMe·C_5H_{11}-*n* in presence of NHPhMe–MgEtBr affords n-*amyl* β-n-*amyl*iso*propenyl ketone*, b.p. 140°/13 mm.; this with CHNa$(CO_2Et)_2$ (**VI**) followed by hydrolysis yields 5-*methyl*-2-*butyl*-5-n-*amyl*cyclo*hexane*-1 : 3-*dione*, m.p. 72—73°, whilst with CN·CHNa·CO·NH_2 (**VII**) δ-keto-β-methyl-β-*n*-amyldecoic acid (*Et* ester, b.p. 185—188°/12 mm.; semicarbazone, m.p. 98°), is obtained. Similarly COMe·$C_{10}H_{21}$-*n* condenses to give *n*-decyl β-*n*-decyl-*iso*propenyl ketone; this with (**VI**) affords 5-*methyl*-2-n-*nonyl*-5-n-*decyl*cyclo*hexane*-1; 3-*dione*, m.p. 69°, and with (**VII**) yields δ-keto-β-methyl-β-*n*-decylpentadecoic acid (*Et* ester, b.p. 245—250°/12 mm.). W. C. J. R.

Long-chain acids. IV. P. C. Mitter and B. K. Bhattacharyya (*J. Indian Chem. Soc.*, 1942, **19**, 69—75).—Unsaturated acids of the type necessary for the synthesis of civetone have been prepared by a new process. Hydrolysis (KOH) of shellac affords aleuritic acid [θιο-trihydroxyhexadecoic acid] (**I**), m.p. 100—101°, which with P_2I_4 in CS_2–Et_2O gives o-*iodo*-Δ^9-*hexadecenoic acid* (**II**). (**II**) (Ag salt) in xylene yields the lactone (*epi*ambrettolide), b.p. 165—175°/10 mm. (musk odour). (**I**) is converted into the *Et* ester, m.p. 50—55°, which when treated with P_2I_4 in CS_2 gives *Et* o-*iodo*-Δ^9-*hexadecenoate* (**III**), b.p. 180°/1·5 mm. (**III**) and AcOH–KOAc afford *Et* o-*acetoxy*-Δ^9-*hexadecenoate*, b.p. 190°/2 mm., hydrolysed (KOH–MeOH) to epi*ambrettollic acid* [o-*hydroxy*-Δ^9-*hexadecenoic acid*], m.p. 55—55·5°. Impure (**III**) affords a substance, m.p. 81—82°. (**III**) with CHNa$(CO_2Et)_2$ in C_6H_6 affords, after hydrolysis and decarboxylation of the tricarboxylic ester and re-esterification, *Et* Δ^9-*hexadecene*-αο-*dicarboxylate* [*Et homocivetate*], (**IV**), b.p. 210—215°/3 mm. A similar condensation in EtOH gives *Et* o-*ethoxy*-Δ^9-*hexadecenoate*, b.p. 156°/1 mm. (**IV**) is hydrolysed to homocivetic acid, m.p. 102·5—103·5°. (**III**) with KCN in EtOH gives *Et* o-*cyano*-Δ^9-*hexadecenoate*, b.p. 190°/1 mm. A partial synthesis of (**I**) has been achieved. (**III**) with NaOPh in EtOH yields *Et* o-*phenoxy*-Δ^9-*hexadecenoate*, m.p. 41—43°, b.p. 233—237°/3 mm., hydrolysed to the *acid*, m.p. 59° (**V**). Et o-phenoxy-ι-ketopalmitate (cf. A., 1940, II, 203) could not be reduced, dehydrated, and hydrolysed to (**V**). C. S.

Halogenation of fatty acids. I. Reaction between bromine and the silver salts of higher fatty acids. II. Reaction between halogens and metallic salts of higher fatty acids. T. N. Mehta, V. S. Mehta, and V. B. Thosar (*J. Indian Chem. Soc., Ind. Ed.*, 1940, **3**, 137—143, 166—173).—I. Dry Ag salts of stearic (**I**), palmitic (**II**), myristic, and lauric acids with Br in CCl_4 give respectively hepta- (**III**), penta- (**IV**), tri- (**V**), and un-decyl bromide in 60—86% yield; (**I**) gives also a small amount of the $C_{17}H_{35}$ ester. (**III**), (**IV**), and (**V**) with C_5H_5N give the quaternary salts, whilst (**III**) with Ag_2O and H_2O yields $C_{17}H_{35}$·OH. (**IV**) is converted into the ester by treatment with Ag palmitate, and with KCN and KI in EtOH yields $C_{15}H_{31}$·CN.

II. I (2 mols.) and Ag palmitate in CCl_4 yield $C_{15}H_{31}I$; the use of <2 mols. of I gives lower yields of $C_{15}H_{31}I$ and larger quantities of (**II**) and its $C_{15}H_{31}$ ester. The Hg and Pb salts are less active than the Ag salt towards Br and I. The Cu salt does not react. R. J. W. R.

Autoxidation of drying oils. R. S. Morrell, T. R. Bolam, W. R. Davis, S. Marks, E. O. Phillips, and W. S. Sim (*Trans. Faraday Soc.*, 1942, **38**, 362—366).—Criticism of a paper by Farmer and Sundralingam (A., 1942, II, 170). F. L. U.

Autoxidation of oxygen-active acids. III. Tendency of natural triglycerides towards autoxidation and film formation. W. Treibs (*Ber.*, 1942, **75**, [*B*], 632—644; cf. A., 1942, II, 277).—The oil is treated with Br and the bromides are divided into fractions (*A*) insol. in light petroleum (**I**) and insol. or sparingly sol. in Et_2O, (*B*) insol. in (**I**) but sol. in Et_2O, (*C*) sol. in (**I**) but pptd. from Et_2O by a little MeOH, and (*D*) sol. in (**I**) and not pptd. from Et_2O by a little MeOH. The O_2 absorption of each fraction is measured. It is thus shown that the drying tendency of poppyseed and soya oil is due to glyceryl esters with only 2, that of linseed oil (**II**) to glycerides with 2 and with 3, O_2-active acid chains. The autoxidisability of a glyceride is an additive function of the O_2-consuming power of its active acid residues. Autoxidation of Me esters and of glycerides is accompanied by loss of H_2O and drying is therefore possibly an auto-oxy-condensation. It is recommended that the evaluation of drying oils, particularly of (**II**), should be based on the wt. of the Br adducts insol. in (**I**) obtained from 100 g. of oil. H. W

Action of hydrogen peroxide on glycollic acid. H. S. Fry and K. L. Milstead (*Proc. Iowa Acad. Sci.*, 1935, **42**, 124—125).—Previous observations on " perhydrolysis " (cf. A., 1931, 819) are extended to the action of H_2O_2 on glycollic acid. CH. ABS. (*e*)

Pyrolysis of lactic acid derivatives. Conversion of methyl α-acetoxypropionate into methyl acrylate.—See B., 1942, II, 273.

Synthesis of methyl α-methoxyacrylate and α-methoxyacrylonitrile. Characterisation of methoxy-derivatives of propionic acid. J. W. Baker (*J.C.S.*, 1942, 520—522).—$CH_2Cl{\cdot}CHCl{\cdot}CO_2Me$ and NaOMe (1 mol.) yield *Me α-chloro-β-methoxypropionate* (**I**), b.p. 65·5—66°/11 mm. (*amide*, m.p. 61°), also obtained from $OH{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2Me$. $OMe{\cdot}CH_2{\cdot}CO_2Me$ and HCO_2Me with mol. Na in C_6H_6 yield $ONa{\cdot}CH{:}C(OMe){\cdot}CO_2Me$, which on acidification and reduction (Raney Ni) gives $OH{\cdot}CH_2{\cdot}CH(OMe){\cdot}CO_2Me$ (**II**); this with aq. NH_3 yields *β-hydroxy-α-methoxypropionamide*, m.p. 71°. (**II**) with $SOCl_2$–C_5H_5N affords $CH_2Cl{\cdot}CH(OMe){\cdot}CO_2Me$, converted by aq. NH_3 into *β-chloro-α-methoxypropionamide*, m.p. 138°. $CH_2Br{\cdot}CHBr{\cdot}CO_2Me$ and NaOMe [2 mols., then 1 mol. with p-$C_6H_4(OH)_2$] yield a product which on acidification and esterification (Ag_2O–MeI) gives *Me αβ-dimethoxypropionate*, b.p. 74·5°/14 mm. (*amide*, m.p. 58°). Paraldehyde, MeOH, and HCl give $CHMeCl{\cdot}OMe$, which with Br yields $CH_2Br{\cdot}CHBr{\cdot}OMe$; this with CuCN in dry Et_2O affords *β-bromo-α-methoxypropionitrile* (**III**), b.p. 84—89°/16 mm., which with HCl–MeOH–Et_2O at −10° gives the *imino-ether hydrochloride*, decomposed (*a*) on warming into *β-bromo-α-methoxypropionamide* (**IV**), m.p. 135°, (*b*) with ice into *Me β-bromo-α-methoxypropionate* (**V**), b.p. 49°/0·5 mm. $OMe{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2Me$ and aq. NH_3 afford *α-bromo-β-methoxypropionamide*, m.p. 84°. (**III**) in boiling C_5H_5N gives *α-methoxyacrylonitrile*, b.p. 27·5°/15 mm., 32·5°/23 mm., which with HCl–MeOH–Et_2O followed by warming gives *αα-dimethoxypropionamide*, m.p. 117°, also obtained by the action of aq. NH_3 on $CMe{\cdot}(OMe)_2{\cdot}CO_2Me$. (**V**) in Et_2O with piperidine–quinol affords $CH_2{:}C(OMe){\cdot}CO_2Me$, which with aq. NH_3 gives *α-methoxyacrylamide* (**VI**), m.p. 109°, also obtained from (**IV**) and NH_3–MeOH. (**VI**) with Br–CCl_4 affords *αβ-dibromo-α-methoxypropionamide*, m.p. 106°. W. C. J. R.

Preparation, enol-determination, and fission of ethyl α-butyrylacetoacetate. J. Pascual and F. Buscaróns (*Anal. Fís. Quím.*, 1941, **37**, 384—391).—$COPr{\cdot}CHAc{\cdot}CO_2Et$ in Et_2O heated with NH_3 yields NH_2Ac and $PrCO{\cdot}NH_2$. Br titration and n show that it contains 90% of the enolic form. F. R. G.

Preparation of dibasic acids from petroleum distillates.—See B., 1942, II, 273.

Erucic acid. Preparation of erucic acid. General oxidation reactions. Oxidation with gaseous oxygen. C. Dorée and A. C. Pepper (*J.C.S.*, 1942, 477—483).—Erucic acid (**I**), m.p. 33·8°, is obtained in 25—30% yield from rapeseed oil, solid fatty acid impurities being removed by pptn. as Pb salts. (**I**) in H_2O_2–AcOH at 100° affords *μν*-dihydroxybehenic acid (**II**), m.p. 101°, whilst brassidic acid (**III**) yields the isomeride (**IV**), m.p. 132°; in presence of OsO_4 (**I**) yields (**IV**) whilst (**III**) gives (**II**). The *cis*-relationship of (**II**) is supported by its higher rate of reaction with $Pb(OAc)_4$. With alkaline $KMnO_4$ (**I**) yields (**IV**) whilst (**III**) gives (**II**), both in 80—90% yields. K erucate with neutral $KMnO_4$ affords (**IV**) and the two keto-hydroxybehenic acids isolated as semicarbazones, m.p. 134° and 157·5°. (**I**) with BzO_2H yields 60—70% of oxidoerucic acid (**V**), hydrolysed (HCl, EtOH, H_2O) to (**II**) whilst (**III**) affords oxidobrassidic acid (**VI**), hydrolysed to (**IV**). KIO_4 or $Pb(OAc)_4$ converts (**II**) and (**IV**) into nonaldehyde (**VII**) and brassylic semialdehyde. Me erucate (**VIII**) with H_2O_2–AcOH at 100° gives *Me μν-dihydroxybehenate*, m.p. 78°, hydrolysed to (**II**); Me brassidate (**IX**) similarly yields an *isomeride*, m.p. 111°, hydrolysed to (**IV**). With BzO_2H (**VIII**) yields *Me oxidoerucate* (**X**), m.p. 28°, and (**IX**) affords *Me oxidobrassidate*, m.p. 42·3°. (**VIII**) with $Pb(OAc)_4$ yields (**VII**) and a *compound*, m.p. 51·8°, possibly Me brassylate semialdehyde. At 70° with O_2 (**I**) gives (**V**) whilst at 120° or at 70° in Ac_2O it yields (**VI**); hydrolysis of the oxidation products gives (**IV**). (**VIII**) with O_2 at 70° in presence of Co erucate yields (**X**) and a complex hydrolysed to (**IV**). (**V**) and (**VI**) are relatively resistant to hydrolysis. W. C. J. R.

Preparation of tartaric acid from carbohydrates.—See B., 1942, II, 277.

Hydrolysis of thiolactones and lactonisation of thiol-acids. E. Schjånberg (*Ber.*, 1942, **75**, [*B*], 468—482).—The behaviour of $SH{\cdot}[CH_2]_3{\cdot}CO_2H$, $SH{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$, $SH{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}CO_2H$ (**I**), $SH{\cdot}CHEt{\cdot}[CH_2]_2{\cdot}CO_2H$ (**II**), $SH{\cdot}[CH_2]_4{\cdot}CO_2H$ (**III**), and the corresponding lactones has been investigated. Generally the velocity coeff. of lactonisation and of acid hydrolysis can be very exactly determined. With (**I**) and (**II**) and the corresponding thiolacetones, *i.e.*, with S attached to *tert.* C, different conditions of equilibrium are reached by lactonisation and acid hydrolysis. (**III**) is stable in that it does not become lactonised in H_2O and the hydrolysis of δ-thiovalerolactone is complete. Changes of temp. cause alterations in the velocity and displacements of the equilibrium. Comparison of the rates of hydrolysis of a given thiolactone with varying concn. of catalyst acid shows that for γ-thiolactones the observed coeffs. $k_h + k_l$ are exactly ∝ concn. of catalyst acid. This is true also for γ-SH-acids whereas δ-thiolactones are sensibly hydrolysed by H_2O. Alkyl substitution at C attached to S increases the velocity coeff. $k_h + k_l$; CO_2H in β-position to S diminishes the coeff. to ~1/2. δ-Thiolactones are much more rapidly hydrolysed by acids than the corresponding γ-thiolactones. In alkaline solution velocity coeffs. cannot be observed. Autocatalysis occurs invariably in H_2O. H. W.

Mechanism of the catalytic reduction of carbonyl compounds. L. C. Anderson and N. W. MacNaughton (*J. Amer. Chem. Soc.*, 1942, **64**, 1456—1459).—Raman spectra are used to prove the existence of C–D or O–D linkings in the products obtained by catalytic treatment of aldehydes and ketones with 4 : 1 H_2–D_2. Addition, $COR{\cdot}CH_2R' \rightarrow OD{\cdot}CDR{\cdot}CH_2R'$, occurs when Pr^aCHO, $COMe_2$, MeCHO, $COEt_2$, or COMeEt is " deuterated " in presence of Pt or Ni at 25°, but at 200—250° in presence of Pt, Ni, or Cu chromite Pr^aCHO and $COMe_2$ react mostly as enol, thus: $COR{\cdot}CH_2R' \rightarrow OH{\cdot}CR{:}CHR' \rightarrow OH{\cdot}CDR{\cdot}CHDR'$. At 150° in presence of Pt or Cu chromite Pr^aCHO reacts mostly as ketone. OH of $Pr^\beta OH$ or Bu^aOH is convertible into OD in presence of Ni at 25° or Pt at ≯250°. In presence of Ni or Cu chromite at 250°, α- and β-H of $Pr^\beta OH$ and Bu^aOH are replaceable by D, indicating that dehydrogenation, enolisation, and hydrogenation occur in the above exchange reactions. R. S. C.

Equilibrium of formaldehyde with glycine and alanine. E. Baur (*Helv. Chim. Acta*, 1942, **24**, 1018—1025; cf. A., 1940, I, 213).—Measurements of the f.p. of solutions of glycine (**I**) in CH_2O and of the solubility of (**I**) in solution of CH_2O give the complex const., $K = 0{\cdot}805$. The similar const. for alanine (**II**) is 0·12. The acidity of solutions of (**I**) and (**II**) in CH_2O diminishes rapidly as the dilution increases. Equilibrium between CH_2O and (**I**) or (**II**) is very rapidly reached. H. W.

Preparation of aliphatic αβ-unsaturated aldehydes. P. Karrer and A. Epprecht (*Helv. Chim. Acta*, 1942, **24**, 1039—1045).—Phytyl bromide is converted into phytylpyridinium bromide, which is condensed with p-$NO{\cdot}C_6H_4{\cdot}NMe_2$ to the nitrone, hydrolysed by 2N-HCl to *phytenal* (**I**), b.p. 157°/0·3 mm., which gives the typical aldehyde reactions. Similarly, farnesyl bromide is transformed through the (non-isolated) intermediates into farnesal (**II**) (semicarbazone, m.p. 133°), and *βζκ-trimethyl-*Δ^a*-dodecaenal*, b.p. 150°/11 mm., 102°/0·2 mm., is derived from the corresponding bromide. The main difficulty is caused by the impossibility of converting the highly unsaturated alcohols into the corresponding homogeneous bromides. This difficulty does not arise when, *e.g.*, farnesol is transformed by C_5H_5N and p-$C_6H_4Me{\cdot}SO_2Cl$ into *farnesylpyridinium p-toluenesulphonate*, which is condensed with p-$NO{\cdot}C_6H_4{\cdot}NMe_2$ and then hydrolysed to (**II**). Similarly, geranylpyridinium p-toluenesulphonate is transformed into citral. Phytol is transformed by $Al(OBu^\gamma)_3$ in boiling $COMe_2$–C_6H_6 into *ζκξσ-tetramethyl-*$\Delta^{\gamma\epsilon}$*-nonadecadien-β-one*, b.p. 160—172°/0·35 mm., which does not show aldehydic reactions and results from the condensation of primarily formed (**I**) with $COMe_2$. H. W.

Absorption spectrum of a βγ-unsaturated aldehyde.—See A., 1942, I, 351.

Manufacture of ketals.—See B., 1942, II, 277.

Abnormal Grignard reactions. X. Enolising and reducing action of Grignard reagents on di*iso*propyl ketone. F. C. Whitmore and R. S. George. **XI—XIII. Sterically hindered aliphatic carbonyl compounds. I. Ketones containing the methyl*tert.*-butylneopentylcarbinyl group and their bromo-magnesium enolates.** F. C. Whitmore and D. I. Randall. **II. Ketones containing the dineopentylcarbinyl group. III. Compounds derived from the bromo-magnesium enolates of alkyl dineopentylcarbinyl ketones.** F. C. Whitmore and C. T. Lester (*J. Amer. Chem. Soc.*, 1942, **64**, 1239—1242, 1242—1246, 1247—1251, 1251—1253; cf. A., 1941, II, 162).—X. Contrary to Smith *et al.* (A., 1937, II, 293), the enolisation of CORR' by MgR''X is much influenced by the nature of R''. Hindrance in R'' decreases the amount of addition; the nature and no. of H on $C_{(\beta)}$ of R'' determine the amount of reduction. Enolisation, reduction, and addition occurring by interaction of $COPr^\beta_2$ with MgR''Br are R'' = Me 0, 0, 95, Et 2, 21, 77, Pr^a 2, 60, 36, Pr^β 29, 65, 0, Bu^β 11, 78, 8, CH_2Bu^γ 90, 0, 4%, respectively. With $MgBu^\gamma Br$, 65% of reduction occurs.

XI. $CH_2Bu^\gamma{\cdot}CMeBu^\gamma{\cdot}COCl$ (**I**) and MgRBr (excess) in Et_2O give *Me* (**II**) (91%), b.p. 55°/3 mm., *Et* (**III**) (79%), m.p. 15°, b.p. 85°/5 mm., and *Pr*$^\beta$ *αγγ-trimethyl-α-*tert.*-butyl-*n*-butyl ketone* (**IV**) (58%), m.p. 38—39°, b.p. 77—87°/6 mm., as sole products. In Bu_2O at 140°, (**II**), (**III**), and (**IV**) show no addition but 94, 57, and 25%, respectively, of enolisation occurs. Steric hindrance of (**II**), (**III**), and (**IV**) is great: semicarbazones and 2 : 4-dinitrophenylhydrazones are not obtained. (**II**) could not be reduced (H_2–Raney Ni at 250°/3000 lb. causes some cleavage) and gives no haloform reaction; oxidation of (**II**) to $CH_2Bu^\gamma{\cdot}CMeBu^\gamma{\cdot}CO_2H$ by CrO_3–AcOH occurs only at ≮90°. With MgEtBr in Et_2O, the ketones give enolates, that from (**II**) being pptd.; with CO_2, these give the derived acids, which, when heated, give CO_2 and the original ketones; with R'COCl

the enolates from (II) and (III) give $CH_2Bu^{\gamma}\cdot CMeBu^{\gamma}\cdot CO\cdot CHR\cdot COR'$, but with BzCl the enolate of (IV) gives *γ-benzoyloxy-ββζζ-tetramethyl-δ-tert.-butyl-Δ$^{\beta}$-n-heptene* (72%), m.p. 50—52°, b.p. 177—180°/8 mm., readily hydrolysed by hot KOH–EtOH to BzOH and (IV); the enolate of (III) with PhCHO gives *α-phenyl-ββζζ-tetramethyl-δ-tert.-butyl-n-heptan-α-ol-γ-one* (V) (26%), m.p. 90—92°, but those of (II) and (IV) do not react thus. *εηη*-Trimethyl-ε-*tert.*-butyl-*n*-octane-ββδ-, an oil (2 : 4-*dinitrophenylhydrazone*, m.p. 181—182°; Cu derivative, m.p. 166—168°), *α-phenyl-δζζ-trimethyl-δ*-tert.-*butyl*-n-*heptane-αγ-*, m.p. 87—88·5°, b.p. 205—210°/8 mm. (2 : 4-dinitrophenylhydrazone, m.p. 186—187°; Cu derivative, m.p. 135—137°), *ββδθκκ-hexamethyl-δθ-di*tert.-*butyl*-n-*undecane-εη-*, m.p. 128—130°, *ηα*-trimethyl-*γγ*-diethyl-*η-tert.*-butyl-*n*-decane-*δζ-*, m.p. 129—131°, and *α-phenyl-ββζζ-tetramethyl-δ*-tert.-*butyl*-n-*heptane-αγ-*, m.p. 115—116°, b.p. 166—169°/3 mm., *-dione*, $CH_2Bu^{\gamma}\cdot CMeBu^{\gamma}\cdot CO\cdot CH_2\cdot CO\cdot CH(CH_2Bu^{\gamma})_2$ [also obtained from (I) and $(CH_2Bu^{\gamma})_2CH\cdot CO\cdot CH_2\cdot MgBr$ or from $(CH_2Bu^{\gamma})_2CH\cdot COCl$ and $CH_2Bu^{\gamma}\cdot CMeBu^{\gamma}\cdot CO\cdot CH_2\cdot MgBr$], $CH_2Bu^{\gamma}\cdot CMeBu^{\gamma}\cdot CO\cdot CH_2\cdot CO_2H$, m.p. 116—117°, $CH_2Bu^{\gamma}\cdot CMeBu^{\gamma}\cdot CO\cdot CHMe\cdot CO_2H$, m.p. 121—123°, and $CH_2Bu^{\gamma}\cdot CMeBu^{\gamma}\cdot CO\cdot CMe_2\cdot CO_2H$, m.p. 100—102°, are described. With $K_2Cr_2O_7$ in boiling dil. H_2SO_4, (V) gives $CH_2Bu^{\gamma}\cdot CMeBu^{\gamma}\cdot CO\cdot CHMe\cdot COPh$, m.p. 114—115°, also obtained from $CH_2Bu^{\gamma}\cdot CMeBu^{\gamma}\cdot CO\cdot CHMe\cdot MgBr$ and BzCl.

XII. $(CH_2Bu^{\gamma})_2CH\cdot COCl$ (VI) and an excess of MgMeBr give, successively, $(CH_2Bu^{\gamma})_2CH\cdot COMe$ (VII), $(CH_2Bu^{\gamma})_2CH\cdot CO\cdot CH_2\cdot MgBr$, and $CH_2[CO\cdot CH(CH_2Bu^{\gamma})_2]_2$ (VIII); addition of (VI) to MgMeBr gives 72% of (VII) and 17% of (VIII), but the reverse addition gives 33% of (VII) and 56% of (VIII). (VII) resembles 2 : 4 : 6 : 1-$C_6H_2Me_3\cdot COMe$: with MgRHal (R = Pr$^{\beta}$, Bu$^{\beta}$, or Bu$^{\gamma}$) it shows 100% enolisation; it gives a 2 : 4-dinitrophenylhydrazone, m.p. 137—138°, extremely slowly and requires long treatment with $Al(OPr^{\beta})$–$Pr^{\beta}OH$ to give $(CH_2Bu^{\gamma})_2CH\cdot CHMe\cdot OH$ (IX), b.p. 113°/20 mm. (3 : 5-dinitrobenzoate, m.p. 97—98°); with NaOBr (4 mols.) in NaOH it gives only *αα-dibromo-εε-dimethyl-γ-β′β′-dimethyl*-n-*propyl*-n-*hexan-β-one*, m.p. 62—63°; with Br (1 mol.) it gives the *α-Br$_1$-ketone*, m.p. 33—34°, converted by KOH–EtOH and then CrO_3–AcOH into $(CH_2Bu^{\gamma})_2CH\cdot CO_2H$; it is readily reduced by Na–EtOH or H_2–Zn–Cu chromite at 200—230°/1500 lb. to (IX). Similar Grignard reactions with (VI) give $(CH_2Bu^{\gamma})_2CH\cdot COEt$ (X) (76%), b.p. 126°/27 mm. [with 10% of diketone; closely resembles (VII) in behaviour; unstable *Br$_1$*-derivative, b.p. 90°/1 mm.], *α-phenyl-* (XI), m.p. 64—65°, -*o*-, m.p. 32—33°, and -*p-tolyl-δδ-dimethyl-β-β′β′-dimethyl*-n-*propyl*-n-*pentan-α-one*, m.p. 78—79°. The aromatic ketones are stable to Br, resistant to oxidation, and do not enolise; therefore, the enol of (VII) is $(CH_2Bu^{\gamma})_2CH\cdot C(OH){:}CH_2$. MgMeI (2 mols.) and (XI) (1 mol.) in boiling Bu_2O give, by normal addition, *β-phenyl-εε-dimethyl-γ-β′β′-dimethyl*-n-*propyl*-n-*hexan-β-ol* (61%), m.p. 42—43°, reconverted into (XI) by oxidation.

XIII. MgBr enolates of (VII) and (X) react as true Grignard reagents: with BzCl they give *α*-phenyl-*ζζ*-di- (XII) (41%), m.p. 73—74° (2 : 4-dinitrophenylhydrazone, m.p. 177—178°), and *β*-phenyl-*βζζ*-tri-methyl-*δ-β′β′*-dimethyl-*n*-propyl-*n*-heptane-*αγ*-dione (XIII) (39%), m.p. 81—82° [also obtained from (XII) by Na–MeI], respectively; with $CH_2Bu^{\gamma}\cdot COCl$ they give $CH_2[CO\cdot CH(CH_2Bu^{\gamma})_2]_2$ (XIV) (*Br$_1$*-derivative, m.p. 87—88°) and $CHMe[CO\cdot CH(CH_2Bu^{\gamma})_2]_2$ (XV) [also obtained from (XIV) by Na–MeI], respectively; with CO_2 they give *β-keto-εε-di-*, m.p. 84—85° (decomp.), and *-αεε-tri-methyl-γ-β′β′-dimethyl*-n-*propyl*-n-*heptoic acid*, m.p. 89—90° (decomp.), respectively, which slowly at room temp. or rapidly when heated regenerate the ketones and CO_2; with $COPh_2$ they give *αα-diphenyl-ζζ-di-* (56%), m.p. 87—88° (with HCl–Et_2O gives the ? chloride, m.p. 73—74°), and *-βζζ-tri-methyl-δ-β′β′-dimethyl*-n-*propyl*-n-*heptan-α-ol-γ-one* (60%), m.p. 122—123° (? chloride, m.p. 110—111°), which with MgMeI give 1 CH_4 at room temp. and a second CH_4 in boiling Bu_2O. With Na–MeI (excess), (XIV) gives *ββζζκκ-hexamethyl-δθ-di-(β′β′-dimethyl*-n-*propyl)*-n-*undecane-εη-dione* (XVI), m.p. 65—66°. The steric effect of CH_2Bu^{γ} is marked (cf. above): cleavage of (XII) and (XIII) requires long boiling in 50% NaOH; (XIV), (XV), and (XVI) are unaffected by boiling in 60% NaOH for 24 hr. (XVI) is the only compound in which the *tert.* H of $(CH_2Bu^{\gamma})_2CH$ reacts as H of an enol (gives 0·63 mol. of CH_4 and adds 1·36 mol. of MgMeI). R. S. C.

Addition of chloroamines to ketens. G. H. Coleman and R. L. Peterson (*Proc. Iowa Acad. Sci.*, 1935, **42**, 122—123).—NCl_3 (but not NH_2Cl) adds to unsaturated hydrocarbons, ketones, and acids to give *C*-chloro-*N*-dichloroamines so that the (+) nature of Cl is > that of NCl_2. NH_2Cl adds to $COPh_2$ to give $CPh_2Cl\cdot CO\cdot NH_2$ but to $CH_2{:}CO$ to yield NHAcCl, whereas NMe_2Cl gives $CPh_2Cl\cdot CO\cdot NMe_2$ and $CH_2Cl\cdot CO\cdot NMe_2$ respectively. CH. ABS. (*c*)

Polymeric amines as an albumin model. Polymeric amine salts and polyethyleneimines.—See A., 1942, I, 363.

Di(amino-acid) derivatives. I. Diglycine–halogen acid additive products. W. S. Frost (*J. Amer. Chem. Soc.*, 1942, **64**, 1286—1287).—Diglycine hydrochloride, $(NH_2\cdot CH_2\cdot CO_2H)_2,HCl$, m.p. 186—187°, is obtained from glycine (I) (2 mols.) and HCl (> 1 mol.) in H_2O or AcOH. An excess of aq. HBr with (I) gives *glycine hydrobromide* (II), hygroscopic, m.p. 143—144°, but 1 mol. each of (I) and (II) give *diglycine hydrobromide*, m.p. 163—165°. An excess of HI with (I) in H_2O or AcOH gives *diglycine hydriodide*, m.p. ~169—170°. R. S. C.

Arginylarginine. K. Felix and H. Schuberth (*Z. physiol. Chem.*, 1942, **273**, 97—102).—Clupeine Me ester hydrochloride is hydrolysed by aq. H_2SO_4 at 37° for 14 days, and the arginylarginine (I) isolated as the *diflavianate*, m.p. 225° (decomp.). *Arginylarginine dipicrate* (sinters 180°, decomp. 185°, then darkens and decomp. 275°) is converted into the dihydrochloride (II) and thence into the *di-picrolonate*, m.p. 285° (decomp.). (II)–BzCl–$NaHCO_3$ give the Bz_2 compound and thence *dibenzoylarginylarginine diflavianate*, m.p. 207° (indef.). Arginylarginine Me ester hydrochloride, decomp. ~180°, then ~220° (sinters 140°), and NH_3–MeOH afford *arginyl-argininеamide trihydrochloride* (corresponding *diflavianate*, decomp. 270°; dipicrate, decomp. 257°). Fission of (I) is effected by peptidase, but not by trypsin; (I) is partly decomposed by arginase. A. T. P.

Acid cleavage of lichen depsides. I. K. Fujii and S. Osumi (*J. Pharm. Soc. Japan*, 1936, **56**, 531—540).—Cleavage is effected by cold conc. H_2SO_4. The cleavage of 8 depsides or their Me ethers is described. CH. ABS. (*c*)

Reactions of formamide with carbonyl compounds. E. Ott (*J. pr. Chem.*, 1941, [ii], **158**, 302).—Concerning priority. R. S. C.

Condensation of malonamide with formaldehyde. W. Röhrs and S. Lang (*J. pr. Chem.*, 1941, [ii], **158**, 109—116).—$CH_2(CO\cdot NH_2)_2$ and aq. CH_2O (0·5—3·0 mols.) at 100° give $CH_2[CH(CO\cdot NH_2)_2]_2$ (I), m.p. 247—248° (decomp.) (identified by hydrolysis by KOH and heating at 220° to give $CO_2H\cdot[CH_2]_5\cdot CO_2H$), and a hygroscopic, H_2O-sol. resin. 3—3·5 mols. of CH_2O gives resins, which after hardening are colourless, clear, tasteless, odourless, stable to org. solvents and cold H_2O, but rapidly attacked by cold acids or alkalis. R. S. C.

Preparation of δδ-dialkylthiosemicarbazides. K. A. Jensen (*J. pr. Chem.*, 1941, [ii], **159**, 189—192).—CS_2 (1 mol.), $NHAlk_2$ (1 mol.), and KOH in aq. EtOH at ≯20° followed by $CH_2Cl\cdot CO_2Na$ yield *dialkylthiocarbamylthiolacetic acids*, $NAlk_2\cdot CS\cdot S\cdot CH_2\cdot CO_2H$ (I) (Alk = *Me*, m.p. 144°; *Et*, m.p. 89°; *Bu$^{\alpha}$*, m.p. 69°). (I) (Na salt) and N_2H_4,H_2O yield *δδ-dialkylthiosemicarbazides* (II) [Alk = *Me*, m.p. 156—157°; *Et* (III), m.p. 84—85°] and some $CS(NH\cdot NH_2)_2$. (III) is also obtained from $NEt_2\cdot CSCl$ and EtOH–N_2H_4,H_2O. (II) are not produced from $NHAlk_2$ and $NH_2\cdot NH\cdot CS\cdot OEt$. C. S.

New methods of preparative organic chemistry. X. Syntheses with diazomethane. B. Eistert (*Angew Chem.*, 1942, **55**, 118—121).—A review.

Preparation of aliphatic [alk]oxy-nitriles.—See B., 1942, II, 278.

II.—SUGARS AND GLUCOSIDES.

Acetylation of carbohydrates in pyridine. A. Leman (*Compt. rend.*, 1942, **214**, 84—87).—With Ac_2O in C_5H_5N at 100°, glucose is 91, galactose 91, sucrose 100, lactose 99 (the max. being reached after 1, 2, ½, and 3 hr., respectively), and starch 1—2% acetylated, but cellulose not at all. A. LI.

Separation of sugars, amino-sugars, and amino-acids. Application to blood group substance. K. Freudenberg, H. Walch, and H. Molter (*Naturwiss.*, 1942, **30**, 87).—Quant. separation of sugars, NH_2-sugars, and acid, neutral, and basic NH_2-acids from one another is achieved by chromatographic adsorption on "acid" and "basic" synthetic resins which act as exchange agents and elution with dil. C_5H_5N, HCl, and aq. NH_3. Human blood group *A* substance, after treatment with $Pb(OAc)_2$ and hydrolysis with acid, yields hexose (chiefly or exclusively *d*-galactose) 20—25, acetylglucosamine ~30, and NH_2-acids (threonine and related compounds) 25—30%. W. McC.

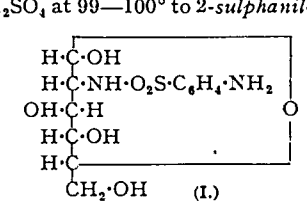
2-Methyl-*d*-altromethylose and its bearing on the configuration of digitalose. F. G. Young, jun., and R. C. Elderfield (*J. Org. Chem.*, 1942, **7**, 241—250).—2-Methyl-α-methyl-*d*-altroside (I) (prep. from 4 : 6-benzylidene-α-methylglucoside described) is converted by successive treatments with CPh_3Cl and Ac_2O in C_5H_5N into 6-*triphenylmethyl-2-methyl-α-methyl*-d-*altroside* 3 : 4-*diacetate*, m.p. 121—121·5°, $[\alpha]_D^{25}$ +63·4° in $CHCl_3$, converted by HBr–AcOH into 2-*methyl-α-methyl*-d-*altroside* 3 : 4-*diacetate*, m.p. 76—77°, $[\alpha]_D^{25}$ +127·8° in $CHCl_3$, and thence by *p*-$C_6H_4Me\cdot SO_2Cl$ in C_5H_5N into the 6-*p-toluenesulphonate*, which does not crystallise. This is transformed by NaI in $COMe_2$ at 100° into 2-*methyl-α-methyl*-d-*altroside* 3 : 4-*diacetate* 6-*iodide* (II), m.p. 54·5—55·5°, $[\alpha]_D^{25}$ +76·2° in $CHCl_3$, converted by reductive hydrolysis (H_2–Raney Ni in alkaline solution) followed by acetylation and then hydrolysis by $Ba(OMe)_2$ into 2-*methyl-α-methyl*-d-*altromethyloside*, b.p. 112—113°/0·55 mm., $[\alpha]_D^{25}$ +91·1° in H_2O, which is hydrolysed by acid to non-cryst. 2-*methyl*-d-*altromethylose* (III), $[\alpha]_D^{25}$ +11·8° in H_2O; this reduces Fehling's solution strongly but does not yield a cryst. phenyl-, *p*-bromo-, *p*-nitro-, or 2 : 4-dinitrophenyl-, or *p*-toluenesulphonyl-hydrazone. (I), *p*-$C_6H_4Me\cdot SO_2Cl$, and C_5H_5N at 0° give the non-cryst. 6-*p-toluenesulphonate* and thence the

non-cryst. 6-*iodide* and (**II**). The oxidation of (**III**) by Br–H_2O and $Ba(OI)_2$ is described. (**III**) is not identical with the enantiomorph of digitalose (**IV**). It is suggested that 2-methyl-*d*-galomethylose, the only possible structure for (**IV**) remaining on the basis of hitherto accepted work, is open to question. 2-Methyl-*l*-rhamnose, m.p. 113—114°, has now been obtained cryst. B.p. and m.p. are corr. H. W.

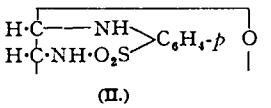
Influence of lyotropic substances on the specific rotation of β-glucosan.—See A., 1942, I, 353.

Rotational relationships of alkyl glucosides. L. C. Kreider and E. Friesen (*J. Amer. Chem. Soc.*, 1942, **64**, 1482—1483).—The following data are recorded, those in parentheses referring to the tetra-acetates: β-*n*-propyl-, m.p. 102·5—103·5°, $[\alpha]_D$ −39·5° in H_2O (m.p. 103°, $[\alpha]_D$ −21·3° in $CHCl_3$), β-*n*-butyl-, m.p. 66—67°, $[\alpha]_D$ −37·4° in H_2O (m.p. 65—66°, $[\alpha]_D$ −21·2° in $CHCl_3$), β-n-*amyl*-, m.p. 89·5—90°, $[\alpha]_D$ −35·7° in H_2O (m.p. 46—47°, $[\alpha]_D$ −21·5° in $CHCl_3$), β-n-*heptyl*-, m.p. 76—78°, $[\alpha]_D$ −33·1° in H_2O (m.p. 68·0—68·5°, $[\alpha]_D$ −19·7° in $CHCl_3$), β-iso*propyl*-, m.p. 128·5—129·5°, $[\alpha]_D$ −37·6° in H_2O (m.p. 136—137°, $[\alpha]_D$ −22·9° in $CHCl_3$), β-iso*butyl*-, m.p. 113—114°, $[\alpha]_D$ −38·2° in H_2O (m.p. 122·5—130°, $[\alpha]_D$ −20·2° in $CHCl_3$), β-*tert*.-butyl- (m.p. 148°, $[\alpha]_D$ −12·8° in $CHCl_3$), β-*n*-hexyl- ($[\alpha]_D$ −20·0° in $CHCl_3$), β-*n*-nonyl- ($[\alpha]_D$ −19·3° in $CHCl_3$), β-*n*-decyl ($[\alpha]_D$ −18·6° in $CHCl_3$), and β-*n*-dodccyl- ($[\alpha]_D$ −16·6° in $CHCl_3$) -glucoside. These and literature data show that $C_{>3}$-alkyl-β-*n*-glucosides have $[M]_D$ 8700—9200 in H_2O and their acetates $[M]_D$ 8300—9200 in $CHCl_3$. M.p. are corr. R. S. C.

New type of sulphanilamide derivative of *d*-glucose. 2-Sulphanilamido-α-*d*-glucose and derivatives. E. L. Jackson (*J. Amer. Chem. Soc.*, 1942, **64**, 1371—1374).—*d*-Glucosamine hydrochloride, *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$, and $NaHCO_3$ in aq. $COMe_2$ at 25° give 2-N^4-*acetylsulphanil*-, m.p. (+*x*H_2O) variable, 180—182°, (anhyd.) 192—193°, $[\alpha]_D^{20}$ (anhyd.) +21·2° → +10·1° in H_2O, hydrolysed by 0·5N-H_2SO_4 at 99—100° to 2-*sulphanil-amido*-α-d-*glucose* [(**I**) or the pyranose form], m.p. 202° (decomp.), $[\alpha]_D^{20}$ +24·5° → +14·4° in H_2O (isolated as hydrochloride and regenerated therefrom by Ag_2CO_3 in MeOH). Pure or syrupy (**I**) in 50% aq. AcOH at room temp. gives 2-*sulphanilamido*-N-d-*glucoside* [(**II**) or the pyranose form], +2H_2O, darkens from 235—240° to 275°, and anhyd., $[\alpha]_D^{20}$ (anhyd.) +119·7° (const.) in H_2O, which does not reduce Fehling's solution and is not diazotisable until hydrolysed (reaction in 0·1N-HCl complete in 1 hr. at 100°). (**I**) has no bacteriostatic or pharmacological action and is not rapidly absorbed. R. S. C.



(I.)



(II.)

Synthesis of cellobiose. W. T. Haskins, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 1289—1291).—*epi*Cellobiose octa-acetate (A., 1942, II, 80) with 30% aq. HBr in Ac_2O–AcOH at 20° and later 5° gives acctobromo*epi*cellobiose, reduced by Zn dust and a trace of H_2PtCl_6 in aq. AcOH to cellobial hexa-acetate. Oxidation by BzO_2H in EtOAc then gives a syrup, converted by Ac_2O–C_5H_5N at room temp. into mixed α- and β-cellobiose octa-acetates (63%), m.p. 180—185°, which with $Ba(OMe)_2$–MeOH gives cellobiose (35%). This is a total synthesis. R. S. C.

Synthesis of lactose and its epimeride. W. T. Haskins, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 1490).—Synthesis of *epi*lactose and thence of lactose from *iso*propylidene-*D*-mannosan and acetobromo-*d*-galactose (cf. preceding abstract) is announced without details. R. S. C.

***D*-Mannosan<1, 5>β<1,6> from β-phenyl-*d*-mannoside.** E. M. Montgomery, N. K. Richtmyer, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 1483—1484).—*d*-Phenyl-*D*-mannoside in boiling 2·6N-KOH gives a syrup, converted by Ac_2O–C_5H_5N into *D*-mannosan<1, 5>β<1, 6> 2 : 3 : 4-triacetate, whence the mannosan is obtained by a trace of $Ba(OMe)_2$. This renders abs. the synthesis of cellobiose and *epi*cellobiose (see above). R. S. C.

Ganglioside and cerebroside from ox spleen. E. Klenk and F. Rennkamp (*Z. physiol. Chem.*, 1942, **273**, 253—258).—Lipins extracted from ox spleen give a cerebroside fraction (21·6% sugar content), probably a lignoceryl- or behenyl-sphingosin-hexoside (1 : 1 : 1), a cerebroside fraction (37·2% sugar content) of a similar dihexoside (1 : 1 : 2), and ganglioside, $C_{70}H_{130}O_{28}N_2$, decomp. 250° (previous charring and sintering), $[\alpha]_D^{20}$ −3·59° in C_5H_5N, formed probably from lignoceric acid, $C_{24}H_{48}O_2$, sphingosin (**II**), $C_{18}H_{37}O_2N$, and $3C_6H_{12}O_6 + C_{10}H_{19}O_5N$. Fission of the products with aq. HCl affords lignoceric (mainly) + behenic acid (isolated as the Me ester), (**II**) (isolated as sulphate), and galactose + glucose. A. T. P.

Steroids. XXXI. Glucoside formation from epimeric alcohols. K. Miescher, C. Meystre, and J. Heer (*Helv. Chim. Acta*, 1941, **24**, 988—998).—Repetition of previous work (A., 1938, II, 174) shows that certain *epi*-compounds give β-glucosides which are difficult to crystallise. Coprosterol, acetobromoglucose, and dry Ag_2O in Et_2O at room temp. afford coprosterol-β-glucoside tetra-acetate, m.p. 198—200°, hydrolysed by NaOMe in MeOH at 20° to *coprosterol β-glucoside* (+H_2O), m.p. 175° and 215° after partial solidification. Similarly prepared are the *β-glucoside tetra-acetates* of *epi*coprosterol, m.p. 140—141° [free *glucoside* (+1H_2O), m.p. 188—193°], *t*-cholestanol, m.p. 174—175°, *epi*cholestanol, m.p. 170—172°, *t*-androsterone, m.p. 191—192°, *c*-androsterone, m.p. 154° and 179—181° after re-solidification (free *-glucoside*, m.p. 228—229°), *t*-borneol, m.p. 119—120°, *iso*borneol, m.p. 113—115°. H. W.

Synthesis of a phloracetophenone glucoside, of a naringenin glucoside, and of *p*-phloridzin. G. Zemplén and R. Bognár (*Ber.*, 1942, **75**, [*B*], 645—649).—Phloracetophenone and acetobromoglucose are condensed by NaOH in aq. $COMe_2$ to 4-*phloracetophenone-glucoside tetra-acetate* (**I**), m.p. 215—216°, softens at 213°, $[\alpha]_D^{20}$ −52·7° in C_5H_5N, which gives 2 : 6 : 1 : 4-$(OMe)_2C_6H_2Ac{\cdot}OH$ when methylated (CH_2N_2) and then hydrolysed. With *p*-$OH{\cdot}C_6H_4{\cdot}CHO$ in strongly alkaline solution (**I**) affords 4′-*naringeninglucoside* (+1·5H_2O), m.p. ~155—160° after softening at 110° or (anhyd.), m.p. 191°, $[\alpha]_D^{25}$ −78·0° in 96% EtOH, −40·4° in C_5H_5N, hydrolysed by dil. acid to glucose and naringenin, m.p. 247—248° (decomp.), softens at 245°. (**II**) is hydrogenated (Pd–C in 96% EtOH) to 4′-*phloretinglucoside* (p-*phloridzin*) (**III**), m.p. 170—173°, softens at 125—130°, $[\alpha]_D^{14}$ −67·6° in C_5H_5N, −99·5° in 96% EtOH, hydrolysed to phloretin, m.p. 258—259° (decomp.). (**III**), Ac_2O, and C_5H_5N at room temp. yield the *hepta-acetate*, $[\alpha]_D^{15}$ −39·0° in $CHCl_3$, hydrolysed to a non-cryst. phloretin triacetate. H. W.

Rhodeatoxin, m.p. 178°, glucoside from leaf of *Rhodea japonica*, Roth.—See A., 1942, III, 769.

Nitration and denitration of pectin. H. Bock, J. Simmerl, and M. Josten (*J. pr. Chem.*, 1941, [ii], **158**, 8—20).—Increase in the temp. (10—80°) of nitration of apple pectin (1 pt.) by HNO_3 (*d* 1·51; 100 pts.) during 1 hr. decreases the N content (10·6% at 10—20°; 7·2% at 80°), yield, η, and solubility in $COMe_2$. The optimum time of nitration at 20° is 1 hr., reaction being incomplete in <1 hr. and causing degradation after 1 hr. HNO_3 of *d* 1·52 gives the best results. The mol. wt. of the part of the product sol. in $COMe_2$ and HNO_3 is 4400 and of that insol. in HNO_3 is 8800. Pectic juices with HNO_3 (~10 pts.) give similar products; hydrolysis is less than expected, but the exact conditions are important. Denitration of nitropectins by $(NH_4)_2S$ or $NH_3 + H_2S$ in $COMe_2$ is incomplete (to 2—3% N) owing to pptn. by added H_2O. Dried nitropectins in aq. suspension give products having 0·2% and freshly pptd. nitropectins give similarly products having 0·09% of N; increase of temp. (5—15° best) or of $[NH_3]$ (3% best) increases degradation. R. S. C.

Formation of polysaccharides containing methoxyl and lignin by the hydrolysis of red beech wood at 100—105°. F. Schütz (*Ber.*, 1942, **75**, [*B*], 703—710).—Exposure of beech wood (**I**) to flowing steam at 100° causes evolution of AcOH which reaches its max. in 3—4 days and then slowly diminishes without ceasing after 10 days. The amount of HCO_2H is relatively small but CO_2 results in appreciable amount. Evolution of CO_2 from (**I**) and H_2O occurs at room temp., the change being chemical and not microbiological. The sum of the products formed invariably exceeds that to be expected from the loss in wt. of the wood, so that H_2O also participates in the reaction. The high OMe content (4·3—10·1%) of the solid extract is remarkable. These extracts are usually colourless, non-hygroscopic substances freely sol. in H_2O, and reduce Fehling's solution more or less readily before hydrolysis. After hydrolysis the reducing power is < expected for a OMe-free sugar. Hydrolysis is accompanied by the separation of lignin-like substances. Possibly the extracts are composed of glucosidic compounds one component of which is aromatic and contains OH and OMe and the other is a carbohydrate. The elementary composition of (**I**) is not appreciably affected by extraction with H_2O. H. W.

Macromolecular compounds. CCLXIII. Cellulose. LXVI. Method of determining carboxyl groups in cellulose, cellulose derivatives, and other polyoses. O. H. Weber (*J. pr. Chem.*, 1941, [ii], **158**, 33—60).—CO_2H in cellulose and its derivatives is determined by base exchange with methylene-blue. The dye solution is percolated in repeated small portions over the fibre (40—250 mg.); the absorbed dye is removed by exhaustive treatment with small portions of dil. HCl; the reversibly bound dye is determined colorimetrically in the acid washings. Single treatments with dye or acid are valueless as equilibria are set up. Other methods (discussed) are theoretically invalid or inaccurate for small amounts. The following ratios, glucose residues : CO_2H, are thus determined: (*a*) cotton wool: native American 1987—2048, hydrocellulose (prep. by $NaHSO_4$) 3210, oxycellulose (prep. by H_2O_2) 918—930 or (prep. by NaOBr) 43 [esterified 4070 and 10,900]; (*b*) wood wool, treated with ClO_2, 100·5—102·3 [after esterification (CH_2N_2) 19,700]; degraded ramie fibre 409—411 [esterified (CH_2N_2) 3330]. R. S. C.

Macromolecular compounds. CCLXVIII. Cellulose. LXVII. Difference between reprecipitated and mercerised celluloses from native fibre celluloses. H. Staudinger and R. Mohr (*J. pr. Chem.*, 1941, [ii], **158**, 233—244).—The degree of polymerisation of repptd. cellulose (cotton, ramie, flax, cellulose regenerated from the acetate) is unaffected by nitration by HNO_3–H_3PO_4, but HNO_3–H_2SO_4 causes degradation which is the more pronounced the larger is the proportion of H_2SO_4. The ratio of the average degree of polymerisation of cellulose nitrate prepared by 2 : 1 H_2SO_4–HNO_3 (*d* 1·48) to that of the nitrate prepared by H_3PO_4–HNO_3 is termed the nitration no. In the above-named cases it is 0·4—0·5. For native fibre cellulose (freed from wax and pectin) it is 0·8—1·0, little or no degradation occurring by either method, and the ratio HNO_3–H_2SO_4 and *d* of the HNO_3 have little effect. The nitration no. is 0·8—1·0 also for hydrocelluloses (prepared from cotton by heating with 2N-$NaHSO_4$ for various times), but nitration appears to give more highly polymerised products. For mercerised cotton, HNO_3–H_3PO_4 causes apparent increase in the degree of polymerisation (greater when more conc. NaOH is used), but the nitration no. is 0·4—0·7; increase in the proportion of H_2SO_4 decreases the nitration no. The results are discussed in light of simultaneous differences in solubility, *X*-ray diagrams, and swelling properties.
R. S. C.

III.—HOMOCYCLIC.

Carotenoids. II. Isomerisation of β-carotene and its relation to carotene analysis.—See A., 1942, III, 787.

Condensation of *cyclo*hexene with halogenobenzenes. R. Pajeau (*Compt. rend.*, 1941, **213**, 655—657).—*cyclo*Hexene (**I**) and PhCl or PhBr, with $AlCl_3$, give 4-chloro- (with a chlorodi*cyclo*hexylbenzene, b.p. 224—226°/15 mm.) or -bromo-phenyl*cyclo*hexane, respectively. *o*- or *p*-C_6H_4MeCl yields 3-, b.p. 149—150°/14 mm., or 5-chloro-2-methylphenyl*cyclo*hexane, b.p. 148—149°/14 mm. (with *x*-chloro-*y*-methyldi*cyclo*hexylbenzene, m.p. 140°), respectively. (**I**) is prepared by dehydrating *cyclo*hexanol vapour, using $BeSO_4$, at 200° (cf. A., 1937, II, 330). A. T. P.

Rubber, polyisoprenes, and allied compounds. II. Molecular-linking capacity of free radicals and its bearing on the mechanism of vulcanisation and photo-gelling reactions. E. H. Farmer and S. E. Michael (*J.C.S.*, 1942, 513—519).—*cyclo*Hexene when heated with Bz_2O_2 (**I**) at 140° in closed vessels yields mainly C_6H_6, BzOH, Δ³-*cyclo*hexenyl benzoate, 3-phenyl-Δ¹-*cyclo*hexene, Δ²′-*cyclo*hexenyl-Δ³-*cyclo*hexene (**II**), 2-Δ²′-*cyclo*hexenyl*cyclo*hexyl benzoate, *cyclo*hexyl benzoate, and phenyl*cyclo*hexyl*cyclo*hexane. (**II**) with Br–$CHCl_3$ gives Δ²′-cyclo*hexenyl*-Δ²-cyclo*hexene tetrabromide*, m.p. 159°, and with O_3–$CHCl_3$ affords n-*octane-αδεθ-tetracarboxylic acid*, m.p. 177°. It is suggested that (**I**) breaks down into radicals Ph· and Bz·O· and these attack the olefine mainly at the α-C but to some extent also at the double linking, initiating interlinking of the mols. and forming benzoates respectively. The action of (**I**) on rubber may be similar, the α-C adjacent to methylated C being attacked. The action of some vulcanisation accelerators is probably due to their power to yield free radicals. S vulcanisation may also involve α-methylenic attack by free radicals. Photo-gelling is promoted by substances undergoing photochemical decomp. to give free radicals.
W. C. J. R.

Attempted synthetic preparation of antirachitic vitamins. V. K. Dimroth, E. Dietzel, and E. Stockstrom (*Annalen*, 1941, **549**, 256—278; cf. A., 1940, II, 133).—γ-1-Hydroxy-2-dimethylaminomethyl-*cyclo*hexyl-Δ^α^-propene (Milas *et al.*, A., 1939, II, 497), b.p. 83—86°/1·5 mm. (? impure; absorption max. at 255 mμ., ε 300), with HBr and then KOH at 175° gives γ-2-dimethylaminomethyl*cyclo*hexylidene-Δ^α^-propene, b.p. 103—106·5°/12 mm. (absorption max. at 237 mμ., ε 17,500), and thence (Hofmann) γ-2-methylene*cyclo*hexylidene-Δ^α^-propene, b.p. 45·5°/5 mm. (absorption max. at 254 mμ., ε 15,000 in Et_2O). With Pd-black at 160° and later 200° this gives *o*-$C_6H_4MePr^n$, consumes 2 O_2 from Bz_2O_2H, gives a resin at 200° (N_2), and polymerises in air; ring-closure could not be induced. *cyclo*Hexylidene-ethyl bromide (**I**) and Mg in Et_2O give *αδ-dicyclohexylidenebutane* (**II**) (poor yield), b.p. 107—108°/6 mm. Simultaneous addition of (**I**) and 2-dimethylaminomethyl*cyclo*hexanone (**III**) to Mg in boiling Et_2O–N_2 gives, *inter alia*, 2-*keto*cyclo*hexylmethyl*cyclo*hexylidene-ethyldimethylammonium bromide*, m.p. 234° [also obtained from (**I**) and (**III**) in Et_2O; converted above the m.p. into the dimeride (semicarbazone, m.p. 195°) of 2-methylene*cyclo*hexanone], cyclo*hexylidene-ethyldimethylamine hydrobromide*, m.p. 207—208° [also obtained from (**I**) and $NHMe_2$], the hydrobromide of (**III**), and a small amount of α-cyclo*hexylidene-β-2-dimethylaminomethyl*-Δ¹-cyclo*hexenylethane* (**IV**), an oil (no absorption at >225 mμ.; formed by dehydration of the 1-OH-compound). Simultaneous addition of *cyclo*hexylidene-ethyl chloride (**V**) (prep. from *cyclo*hexylidene-ethyl alcohol or 1-vinyl*cyclo*hexanol by PCl_3–C_5H_5N), b.p. ~62—72°/11 mm., and (**III**) to Mg in Et_2O, warming, and then keeping at room temp. gives the *hydrochloride*, m.p. 190°, of (**IV**), (**II**), and other compounds. Interaction of (**I**) with Mg in boiling Et_2O–N_2 and addition of (**III**) to the resulting solution gives (**II**) and α-cyclo*hexylidene-β-1-hydroxy-2-dimethylaminomethyl*cyclo*hexylethane* (**VI**), b.p. 108—111°/0·001 mm. (*acetate*, b.p. 95—100°/0·001 mm.), obtained less well by use of (**V**). O_3 converts (**VI**) into *cyclo*hexanone etc.; PBr_3–C_5H_5N–C_4H_6 yields the bromide, which with C_5H_5N gives (**IV**) but with solid KOH at 0° gives α-*cyclo*hexylidene-β-2-dimethylaminomethyl*cyclo*hexylidene-ethane (**VII**) (absorption max. at 232 mμ., ε 11,000 in EtOH). Isomerisation of (**VII**) to (**IV**) occurs on keeping or treating with OH′. Ozonisation of (**IV**) gives *cyclo*hexanone; that of (**VII**) (treatment of the ozonide with Zn dust in AcOH) gives also $(CHO)_2$ and (**III**). Pt at 180° (N_2) converts (**VII**) into phenanthrene and *trans*-$(CHPh{:})_2$. With MeI–Et_2O, (**VII**) gives a *methiodide* (**VIII**), m.p. 177° (absorption max. at 232 mμ., ε 19,000 in EtOH; absorbs 2 H_2). Treating (**VIII**) with Ag_2O–H_2O, removing the H_2O at 40°, and heating at 60° then gives α-*cyclo*hexylidene-β-2-methylene*cyclo*hexylidene-ethane (absorption max. at 260 mμ., ε 15,000 in Et_2O), which absorbs 2·87 H_2 (Pt; AcOH), with O_3 in AcOH gives *cyclo*hexanone and CH_2O, and with $(CH{\cdot}CO)_2O$ in C_6H_6 at room temp. gives 1-cyclo*hexylidenemethyl*-Δ^9:10^-*octahydronaphthalene*-2 : 3-*dicarboxylic anhydride*, m.p. 157°, converted by Pt at 180—200° into $C_{10}H_8$ and β-$C_{10}H_7{\cdot}CO_2H$. (**IV**) gives no cryst. methiodide, but Hofmann degradation (heat at 60°) gives (?) 12-*methyl*-1:2:3:4:5:6:7:8:12:13-*decahydrophenanthrene*, b.p. 68°/0·001 mm. (absorption max. at 265 mμ., ε 11,000, and 275 mμ., ε 9500 in Et_2O), which absorbs 1·2—1·4 H_2 (Pt), with Pt at 180—200° gives phenanthrene, and does not undergo diene addition. R. S. C.

Polymorphism of 1 : 3 : 5-tri*cyclo*hexylbenzene. Dihydroterphenyl. W. Hückel and J. Datow (*J. pr. Chem.*, 1941, [ii], **158**, 295—301).—1 : 3 : 5-Tri*cyclo*hexylbenzene (A., 1940, II, 270) exists in forms, m.p. 68°, ~100°, and 120—127°, but intermediate and less definite m.p. are found due to retained solvent. The structure of dihydroterphenyl (*loc. cit.*; prep. improved), m.p. 152°, is uncertain; *n* (exaltation 2·54—3·30) indicates conjugated ethylenic linkings, but Na in NH_3 causes coloration but no further reduction; at <350° it gives 0·6 H_2 and terphenyl; it is yellow in $C(NO_2)_4$, and with Cl_2–CCl_4 gives a *dichloride*, m.p. ~135—142°, but is indifferent to Br–$CHCl_3$; it is weakly fluorescent (ultra-violet). R. S. C.

Number of isomerides in cyclic organic compounds. M. A. Morro Ramírez (*Anal. Fis. Quím.*, 1941, **37**, 594—603).—The no. of possible permutations for cyclic compounds with univalent substituents of type *X* repeated *a* times, *Y*, *b* times, etc. is $N\,!/a\,!\,b\,!\,c\,!\ldots\ldots$ where $a + b + c \ldots\ldots = N$. F. R. G.

Preparation of styrene by dehydration of phenylmethylcarbinol in gas phase. A. A. Vanscheidt and V. M. Zeltzer (*J. Appl. Chem. Russ.*, 1941, **14**, 521—523).—When CHPhMe·OH (**I**) is passed over Al_2O_3 at 380—400°, the yield of styrene shows a max. (87—88%) when 550—750 g. of (**I**) are used per l. of catalyst per hr. The activity of the catalyst increases in use for, say, 1 hr. and then remains const. for several hr. J. J. B.

Conjugation of a double bond with an aromatic nucleus. II. Addition of anethole to maleic anhydride. M. Lora Tamayo and D. Ayestarán. **III. Condensation of styrene and compounds of the cinnamic series with maleic anhydride.** M. Lora Tamayo and J. M. Viguera (*Anal. Fis. Quím.*, 1941, **37**, 392—396, 397—402; cf. A., 1941, II, 134).—II. Oxidation (alkaline $KMnO_4$) of the additive product of anethole with $(CH{\cdot}CO)_2O$ (**I**) yields *p*-OMe·$C_6H_4{\cdot}CO_2H$ with a OMe-compound, b.p. 46—47°/22 mm., also obtained in addition to $H_2C_2O_4$ from the additively produced acid, thus showing 1 : 2- and 1 : 4-addition for the adduct and 1 : 4-addition for the acid.

III. Styrene in C_6H_6 with (**I**) at 110—120° yields 1-*phenyl*cyclo*butane*-2 : 3-*dicarboxylic anhydride*, m.p. 286—287°, which is oxidised (alkaline $KMnO_4$) to BzOH. $CHPh{:}CH{\cdot}CO_2H$, $CHPh{:}CH{\cdot}CH_2{\cdot}OH$, $CHPh{:}CH{\cdot}CO_2Et$, and $CHPh{:}CH{\cdot}CHO$ do not form adducts. F. R. G.

Liquid sulphur dioxide as solvent medium for chemical reactions. J. Ross, J. H. Percy, R. L. Brandt, A. I. Gebhart, J. E. Mitchell, and S. Yolles (*Ind. Eng. Chem.*, 1942, **34**, 924—926).—The prep. of the following compounds in liquid SO_2 is described: amylbenzenes, $COPh{\cdot}C_{10}H_7$, $COPh_2$, *tert.*-amylphenol, acetoveratrone, PhOBz, $COPh{\cdot}C_6H_4{\cdot}OBz$, *m*-$C_6H_4(OBz)_2$ (by Friedel–Crafts reactions), $PhSO_3H$, m.p. 65°, $C_{12}H_{25}{\cdot}O{\cdot}SO_3H$ (from the alcohol and $ClSO_3H$), *p*-$C_6H_4Br{\cdot}OH$ (from PhOH + Br), $CHPhBr{\cdot}CH_2Br$, and $Ph{\cdot}[CH_2]_2{\cdot}Br$. S. C.

Fluorine derivatives of diphenyl. (Miss) M. W. Renoll (*J. Amer. Chem. Soc.*, 1942, **64**, 1489—1490).—Ph_2 and FSO_3H at 25° or 70° give *diphenyl-4-sulphonyl fluoride* (3·1%), m.p. 76—78°, and -4 : 4′-*disulphonyl fluoride* (high yield), m.p. 197—200° (stable in H_2O or boiling 0·5N-H_2SO_4; converted by $AlCl_3$ into the chloride, m.p. 202—204°). Diazotisation of *o*-$C_6H_4Ph{\cdot}NH_2$ in HCl, conversion into the diazonium fluorosulphonate, decomp. 83—84°, and decomp. thereof at 95° gives 2-*diphenylyl fluorosulphonate*, m.p. 33—34·5°. R. S. C.

Resonance in substituted diphenyls. D. W. Sherwood and M. Calvin (*J. Amer. Chem. Soc.*, 1942, **64**, 1350—1353).—Absorption spectra (recorded) for $PhNO_2$, *o*- and *m*-$C_6H_4Me{\cdot}NO_2$, $(4\text{-}NO_2{\cdot}C_6H_4)_2$ (**I**), m.p. 236·0—236·5° (corr.), 4 : 4′-*dinitro*-3 : 3′- (**II**), m.p. 228·0—

228·5° (corr.), and -2 : 2′-*dimethyldiphenyl* (**III**), m.p. 170°, in EtOH disclose that in the Ph_2 series resonance between the Ph is strong, that displacement of the NO_2 from co-planarity by the 3-Me is reduced by this Ph–Ph resonance, and that repulsion between the 2 : 2′-Me_2 and 6 : 6′-H_2 is insufficient to affect materially the strong Ph–Ph resonance. However, absorption spectra for 4-nitro-4′-amino-diphenyl (**IV**), m.p. 203·5—204° (corr.), -3 : 3′- (**V**), m.p. 142·0—142·5°, and -2 : 2′-*dimethyldiphenyl* (**VI**), m.p. 80—81°, show that Ph–Ph resonance is much stronger with consequent shortening of the 1 : 1′-bond; the 3-Me has still little effect, but the closer proximity of the Ph is such that interference between the 2 : 2′-Me_2 and 6 : 6′-H_2 almost entirely suppresses the resonance. The non-recognition of *cis–trans*-isomerides is discussed. In HCl–EtOH increase in the [HCl] gradually suppresses the absorption of (**IV**), (**V**), and (**VI**), whence are calc. K (=[B][H⁺]/[BH⁺]) for (**IV**) 10·0±1, (**V**) 8·5±1, and (**VI**) 3·0±0·5 × 10^{-4}, in agreement with conclusions above. Preps. are as follows: (**IV**) (35%) from (**I**) by Na_2S_x–EtOH–H_2O; (**II**) (50%) from (3-$C_6H_4Me)_2$ or (25%) by treating diazotised (4 : 3 : 1-$NH_2{\cdot}C_6H_4Me)_2$ with H_2SO_4–$NaNO_2$–Cu powder; (**V**) (28%) from (**II**) by Na_2S_x; (**III**) (31%) from diazotised 5 : 1 : 2-$NO_2{\cdot}C_6H_4Me{\cdot}NH_2$ by CuCl–NH_3–H_2O at 25—30°, and thence (**VI**) (21%). R. S. C.

Reaction of potassium amide in liquid ammonia with diarylbromoethylenes. G. H. Coleman and W. H. Host (*Proc. Iowa Acad. Sci.*, 1935, **42**, 119).—$CR_2{:}CHBr$ (R = *o*- or *m*-C_6H_4Me or -$C_6H_4{\cdot}OMe$) with KNH_2 in liquid NH_3 gives symmetrical tolanes with unaltered orientation of the aromatic nuclei. Ch. Abs. (*c*)

Benzenesulphinic acid and derivatives. S. E. Hazlet and L. C. Raiford (*Proc. Iowa Acad. Sci.*, 1935, **42**, 120).—In *o*-NHR·$C_6H_4{\cdot}OH$ the migration of R from N to O is observed when R = acyl but not when R = sulphonyl. The prep. of $PhSO_2H$, PhSOCl, and 19 sulphinamides and sulphonic analogues is described. Ch. Abs. (*c*)

***o*-Terphenyl (*o*-diphenylbenzene). I. General reactivity, basal structure, and rearrangements of the hydrocarbon.** C. F. H. Allen and F. P. Pingert (*J. Amer. Chem. Soc.*, 1942, **64**, 1365—1371).—Prep. of *o*-$C_6H_4Ph_2$ (**I**), m.p. 58—59°, with other products from PhCl and Na (Bachmann *et al.*, A., 1927, 962) is improved. (**I**) is best crystallised from light petroleum, b.p. 38—40°, at −35°, rising to −10°. It is also obtained by heating the $(CH{\cdot}CO)_2O$ adducts of 3 : 4-diphenyl*cyclo*pentadienone with $Ba(OH)_2$ (18—50%; no isomerides formed), from 1-2′-xenyl-Δ¹-*cyclo*hexene (improved prep.) by chloranil (~20%), and by decarboxylation of $CHPh{:}CH{\cdot}CH{:}C(CO_2H)_2$ (Doebner *et al.*, A., 1902, i, 598; 1907, i, 204; there termed 1 : 2-diphenyl*dicyclo*hexane), but not by various Grignard reactions. It is proposed to number the central ring 1—6 and the terminal rings 1′—6′ and 1″—6″, respectively. The main positions of reactivity (*e.g.*, with Br) are 4′ and 4″, with subsidiary reactivity at 4 and 5. Kekulé bond fixation apparently does not occur; ozonolysis leads mainly to $(CHO)_2$ or, in one experiment, Bz_2, with, sometimes, BzCHO and (?) $C_6(CO_2H)_6$. With a trace of $AlCl_3$ in C_6H_6, (**I**) is rearranged first to *m*- and then to *p*-$C_6H_4Ph_2$ (**II**); 1 mol. of $AlCl_3$ gives only (**II**) and triphenylene (**III**) with traces of Ph_2; $AlCl_3$–NaCl at ~130° gives mainly (**II**), but at ~200° only condensation products including (**III**). The Perrier compound, $BzCl,AlCl_3$, does not cause rearrangement, but gives the 4′-Bz derivative, which with $NaNH_2$ gives (**III**) but no (**I**). R. S. C.

Formation of water-insoluble complexes of α-naphthylamine with metallic thiocyanates and their analytical applications.—See A., 1942, I, 340.

Mechanism of the O. Fischer–Hepp " rearrangement " of nitrosoamines. P. W. Neber and H. Rauscher (*Annalen*, 1942, **550**, 182—195).—Conversion of aromatic *sec.*-nitrosoamines into *p*-NO-derivatives by HCl is proved to occur by liberation of NOCl. NPhMe·NO (**I**) with HCl gives fairly good and with H_2SO_4 very low yields of *p*-NO·$C_6H_4{\cdot}NHMe$ (**II**), but is unchanged by HNO_3. With HBr in Et_2O–EtOH, NPhMe·NO or NPhEt·NO gives only NHPhR,HBr. Addition of (**I**) in Et_2O to $NPhMe_2$ in HCl–EtOH at 0° gives, after 7 days, *p*-NO·$C_6H_4{\cdot}NMe_2$ (**III**) (46%) and NHPhMe but no (**II**); in presence of $NHPh_2$ 86% of 4-*nitrosodiphenylamine* (**IV**), m.p. 143°, and a little (**II**) are formed. $NPh_2{\cdot}NO$ and HCl in presence of $NPhMe_2$ give 47% of (**IV**) and 7% of (**III**), but *p*-NO·$C_6H_4{\cdot}NPh{\cdot}NO$ gives >80% of (**III**) and 85% of (**IV**); 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NMe{\cdot}NO$ and 2 : 4 : 6 :1-$(NO_2)_3C_6H_2{\cdot}NMe{\cdot}NO$ give similarly (**III**) (87 and 72%, respectively) with 2 : 4-di- (88%), m.p. 175°, and 2 : 4 : 6-trinitromethylaniline (90%), m.p. 110°; 2 : 4 : 1-$C_6H_3Me_2{\cdot}NMe{\cdot}NO$ gives (**III**) (74%) and 2 : 4 : 1-$C_6H_3Me_2{\cdot}NHMe$ (58%); 1-nitrosopiperidine gives less easily up to 72·7% of (**III**); 2 : 5 : 1-$CHPh{:}CH{\cdot}C_6H_3(NO_2){\cdot}NMe{\cdot}NO$ gives 4-*nitro*-2-*methylaminostilbene* (84%), m.p. 175°, and (**III**) (50%), but α-$C_{10}H_7{\cdot}NPh{\cdot}NO$ in presence of α-$C_{10}H_7{\cdot}NMe_2$ [*picrate*, m.p. 143° (decomp.)] gives only 4 : 1-NO·$C_{10}H_6{\cdot}NHPh$. Addition of HCl–EtOH to (**I**) and anethole in cold Et_2O gives after 2 days NHPhMe and anethole nitrosochloride. Addition of NOCl–Et_2O to $NPhMe_2$–Et_2O gives after 1 hr. 46% of (**III**). R. S. C.

[Crystal] structure of sulphanilamide.—See A., 1942, I, 355.

Sulphanilamido-aliphatic acids and their salts.—See B., 1942, II, 362.

***p*-Acylamidobenzenesulphonhydroxylamides.**—See B., 1942, III, 222.

Useful solvent for determination of mol. wt. according to Rast.—See A., 1942, I, 358.

Azo-compounds and their intermediates. XXII. Sulphonic acids of polyazobenzenes. P. Ruggli and M. Stäuble (*Helv. Chim. Acta*, 1941, **24**, 1080—1092; cf. A., 1938, II, 318).—$(NPh)_2$ with 20% oleum at 75° and subsequently at 130° gives *p*-NPh·N·$C_6H_4{\cdot}SO_3H$ (+$3H_2O$) whereas with 66% oleum at 95—100° the product is a mixture of about equal parts of the 4 : 4′- [dark red K_2 salt (+$3H_2O$)] and the 4 : 3′-disulphonic acid (yellow K_2 salt), which on reductive fission yield *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$ (**I**) and (**I**) with *m*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$, respectively. 4-(Benzeneazo)azobenzene is converted by 20% oleum at 140° into a tetrasulphonic acid accompanied by considerable carbonisation. With 66% oleum at 60° it gives the 4′ : 4″-*disulphonic acid*, m.p. 157° [*Ca* (+$6H_2O$), K_2, and *Ba* salts] [converted by reductive fission into (**I**) and *p*-$C_6H_4(NH_2)_2$ (**II**)], and a *tetrasulphonic acid*, 2 : 6 : 1 : 4-$(SO_3H)_2C_6H_2(N_2{\cdot}C_6H_4{\cdot}SO_3H$-*p*$)_2$ (K_4 salt), reduced to (**I**) and 1 : 4 : 2 : 6-$(NH_2)_2C_6H_2(SO_3H)_2$. 4 : 4′-Di(benzeneazo)azobenzene with 66% oleum at 55° affords mainly the 4″ : 4‴-disulphonic acid isolated as the K_2 salt (+$4H_2O$), which gives colloidal solutions in H_2O and is reduced to (**I**) (1·6 mols.) and (**II**) (1·8 mols.); the mother-liquors contain a *xx′* : 4″ : 4‴-tetrasulphonic acid, analysed as the *Ca* salt and giving a K_2 salt reduced to (**I**) (1·4 mol.) and 1 : 4 : *x*-$(NH_2)_2C_6H_3{\cdot}SO_3H$ (**III**), showing SO_3H to be present in each nucleus. 4 : 4′-Di(benzeneazobenzeneazo)benzene gives a 4‴ : 4⁗-disulphonic acid, isolated as the K_2 salt which gives turbid viscous solutions in H_2O which gel when cooled; it is reduced exclusively to (**I**) and (**II**). An unisolated tetrasulphonic acid reduced to (**I**), (**II**), and (**III**) occurs in the mother-liquors. The K salts of all sulphonic acids of azo- and disazo-benzene are highly disperse and diffuse rapidly through gelatin whereas the salts of the more complex products diffuse very slowly. The colours of solutions of the azobenzenes and their sulphonic acids in conc. H_2SO_4 are described. Sulphonation of the azobenzenes occurs first in the extreme nuclei; after introduction of SO_3H into each such nucleus it continues towards the centre of the mol. 4-Amino-4′-*p*′-aminobenzeneazohydrazobenzene (Ac_2 derivative, m.p. 218°) is incidentally described. PhNO and (**I**) in boiling C_5H_5N–AcOH afford *p*-NPh·N·$C_6H_4{\cdot}SO_3H$. H. W.

Azo-dyes. II. Soluble derivatives of insoluble azo-dyes. V. N. Ufimtsev (*J. Appl. Chem. Russ.*, 1941, **14**, 600—604).—1 : 2-NAr·N·$C_{10}H_6{\cdot}OH$ (*A*) are esterified with $CH_2Cl{\cdot}COCl$ (**I**) and the esters converted into H_2O-sol. pyridinium salts, which are readily decomposed by alkali to (*A*). 1-Benzeneazo-2-naphthyl chloroacetate with excess of C_5H_5N affords the *pyridinium* salt. 1-(1′-Naphthaleneazo)-2-naphthol with (**I**) in PhMe affords the *chloroacetate*, m.p. 140—140·5°, convertible into a *pyridinium* salt. 1-*p*-Nitrobenzeneazo-2-naphthol similarly gives a *chloroacetate*, m.p. 183·5—184°, forming a pyridinium salt. 1-*Benzeneazo*-2-*naphthyl nicotinate*, m.p. 122·5—123·5° (prep. by nicotinic acid and $SOCl_2$), gives a sol. *methiodide*, which is more stable than the salts described above. G. A. R. K.

Identification of hydrazones and isomeric pyrazolines obtained from αβ-unsaturated ketones. W. J. Peterson and L. C. Raiford (*Proc. Iowa Acad. Sci.*, 1935, **42**, 123—124).—$CHR{:}CH{\cdot}CR'{:}N{\cdot}NHPh$ are distinguished from the isomeric pyrazolines (*A*) by (*a*) reduction (Na–Hg) to NH_2Ph and aliphatic amines, (*b*) rearrangement to (*A*) by hot AcOH, (*c*) cryst. form, (*d*) reduction to $CH_2R{\cdot}CH_2{\cdot}CR'{:}N{\cdot}NHPh$ by Na–Hg in presence of CO_2. Ch. Abs. (*c*)

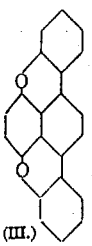
Substituted *cyclo*alkylphenols.—See B., 1942, II, 361.

Derivatives of diphenylyl esters.—See B., 1942, III, 223.

Sesquiterpenes. XLVIII. Synthesis of 5-hydroxy-1 : 6-dimethyl-4-*iso*propylnaphthalene, a contribution to the elucidation of the constitution of guaiol. P. A. Plattner and G. Magyar (*Helv. Chim. Acta*, 1941, **24**, 1163—1166).—Et carvacrylacetate is reduced to β-carvacrylethyl alcohol, which with HBr–AcOH at 100° yields *β-carvacrylethyl bromide* (**I**), b.p. 132—134°/10 mm. $CHMe(CO_2Et)_2$ and (**I**) followed by hydrolysis and decarboxylation give *γ-carvacryl-α-methyl*-n-*butyric acid*, b.p. 188—190°/10 mm., which is converted ($SOCl_2$) into its chloride and then cyclised ($AlCl_3$ in $PhNO_2$ at room temp.) to 1-*keto*-2 : 5-*dimethyl*-7-iso*propyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. This is dehydrogenated by Pd–C at 250—260° to 1 : 6 : 4 : 5-$C_{10}H_4Me_2Pr^{\beta}{\cdot}OH$ [picrate, m.p. 132—133·5°; *compound* with 1 : 3 : 5-$C_6H_3(NO_2)_3$, m.p. 131·5—132°] identical with the product obtained from the unsaturated ketone obtained by loss of H_2O from the $(OH)_2$-ketone derived from guaiol (**II**). The C skeleton and position of the double linking in (**II**) are therefore regarded as established. M.p. are corr. H. W.

Chemical reaction underlying the inhibition by *p*-benzoquinone of

the polymerisation of styrene. W. Kern and K. Feuerstein (*J. pr. Chem.*, 1941, [ii], **158**, 186—199).—CHPh:CH_2 (**I**) and *p*-O:C_6H_4:O (**II**) at 105° give quinol (isolated as quinhydrone) and mixed phenols. After interaction at the b.p. there is isolated a *phenol*, $C_{22}H_{20}O_2$, converted by Me_2SO_4–alkali into mixed ethers including a *Me*$_1$ *ether*, m.p. 158—160°. The reaction is best catalysed by $CCl_3{\cdot}CO_2H$, 1% of which converts (**I**) (4 pts.) and (**II**) (1 pt.) at the b.p. into a saturated *substance*, $C_{22}H_{12-14}O_2$ [? (**III**)] (7%), m.p. 249—250° (and small amounts of substances, m.p. 78—82°, 138—146°, and 84—90°), which, when distilled with Zn, yields a *substance*, $C_{22}H_{12-16}$ (? 1 : 8-4 : 5-*diphenylenenaphthalene*), m.p. 207—210°. (**I**) reacts with CPh_2:CH_2 or 1 : 4-naphthaquinonc, but not with (:CHPh)$_2$,



(III.)

CH_2:CH·OAc, CH_2:CH·CO_2R, CH_2:CR·CO_2R′, CH_2:CH·CN, or anthraquinone. R. S. C.

Fission of phenolic ethers by pyridinium salts. IV. V. Prey (*Ber.*, 1942, **75**, [*B*], 537—546).—The previous view that addition to C_5H_5N causes enhanced reactivity of acids towards phenolic ethers (**I**) does not appear to be universally applicable. The application of H_2SO_4 and HNO_3 is restricted and successful only with polysubstituted ethers. C_5H_5N–H_2SO_4 at 200° splits most (**I**) except Ph_2O with formation of phenolsulphonic acids. C_5H_5N–HNO_3 causes nuclear nitration without fission. $H_2C_2O_4$ is ineffective but 85% and 100% H_3PO_4 are highly active. Fission does not occur with C_5H_5N–$H_2C_2O_4$ or with compounds of C_5H_5N with SO_2 or H_2SO_3. $CCl_3{\cdot}CO_2H$ alone or in presence of C_5H_5N is ineffective. Additive compounds of C_5H_5N with HCO_2H, AcOH, or Ac_2O could not be isolated and fission experiments were unsuccessful. *p*-$NO_2{\cdot}C_6H_4{\cdot}$COCl at 220° transforms *o*-$C_6H_4(OMe)_2$ into *p*-nitrobenzoates of *o*-$C_6H_4(OH)_2$ and *o*-OH·C_6H_4·OMe whereas PhOMe is untouched under these conditions but is largely affected if C_5H_5N is added. AcCl and AcCl–C_5H_5N behave similarly. Scission of *o*-$C_6H_4(OMe)_2$ but not PhOMe is caused by BzCl alone whilst the dark red solution of BzCl in C_5H_5N causes more extensive fission of the former but does not affect the latter. C_6H_4Me·SO_2Cl and $SOCl_2$ resinify and their additive compounds could not be obtained. SO_2Cl_2 has little effect on PhOMe but causes partial fission of *o*-$C_6H_4(OMe)_2$ with production of chlorinated products. SO_2Cl_2–C_5H_5N converts PhOMe into PhOH with traces of C_6H_4Cl·OH and *o*-$C_6H_4(OMe)_2$ into *o*-$C_6H_4(OH)_2$ and *o*-OH·C_6H_4·OMe. $AlBr_3$–C_5H_5N readily brings about fission of most phenolic ethers excepting Ph_2O. C_5H_5N–$ZnCl_2$ causes 50% scission of *o*-$C_6H_4(OMe)_2$, has little effect on PhOMe, and none on diaryl ethers (**II**). C_5H_5N–PCl_5 converts *o*-$C_6H_4(OMe)_2$ and PhOMe mainly into chlorinated products but leaves (**II**) untouched. *p*-$NO_2{\cdot}C_6H_4{\cdot}$COCl,C_5H_5N has m.p. 175° (lit. 228—230°). H. W.

γ-Chloroalkylphenol ethers. L. Bert (*Compt. rend.*, 1941, **213**, 797—798).—PhOMe (10 mols.), CHCl:CH·CH_2Cl (1 mol.) (**I**), and $AlCl_3$ (10 g.) afford 70% of *p*-OMe·$C_6H_4{\cdot}CH_2{\cdot}$CH:CHCl, b.p. 126°/15 mm. *o*-$C_6H_4(OMe)_2$ (2 mols.), (**I**) (1 mol.), and Zn dust (1 g.; $AlCl_3$ unsuitable) yield 3 : 4-*dimethoxy-γ-chloroallylbenzene*, b.p. 162°/15 mm.; 1 : 2 : 3-$C_6H_3(OMe)_3$ affords similarly 3 : 4 : 5-*trimethoxy-γ-chloroallylbenzene*, b.p. 174°/15 mm. OR·$C_6H_4{\cdot}CH_2{\cdot}$CH:CHCl, KOH, and R′OH (1 : 3 : 5 mols.) give OR·$C_6H_4{\cdot}$CH:CH·CH_2·OR′ (R, R′ = alkyl), which are used for the prep. of various natural products (or derivatives). C. S.

Resin phenols. I. Dimerisation of *iso*eugenol methyl ether. A. Müller, M. Raltschewa, and M. Papp (*Ber.*, 1942, **75**, [*B*], 692—703).—Evidence is adduced against the conception of Haworth *et al.* (A., 1931, 954) that di*iso*eugenol Me ether (**I**) is 2 : 3 : 6 : 7-tetramethoxy-9 : 10-diethyl-9 : 10-dihydroanthracene (*A*). Veratrole (**II**), EtCHO, and 90% H_2SO_4 (at >8—10°) or $ZnCl_2$–HCl (no cooling) give 2 : 3 : 6 : 7-*tetramethoxy*-9 : 10-*diethylanthracene*, m.p. 239—240° [in place of the expected (*A*)], which is not identical with (**I**); it is oxidised by HNO_3 or CrO_3–AcOH to 2 : 3 : 6 : 7-tetramethoxyanthraquinone (**III**), m.p. 338—340° (lit. 344°). With 75% H_2SO_4, (**II**) and EtCHO afford αα- 3 : 4 : 3′ : 4′-*tetramethoxydiphenylpropane*, m.p. 76—77°, oxidised by CrO_3 in AcOH to CO[C_6H_3(OMe)$_2$-3 : 4]$_2$, m.p. 144—145°. With 70% H_2SO_4, (**II**) with MeCHO gives 2 : 3 : 6 : 7-*tetramethoxy*-9 : 10-*dimethylanthracene*, m.p. 316° [oxidised (CrO_3 in AcOH at 80° or 40% HNO_3 at 100°) to (**III**)], and with Bu^{β}CHO yields 2 : 3 : 6 : 7-*tetramethoxy*-9 : 10-di*iso*butylanthracene, m.p. 223—224°. 3 : 4 : 1-(OMe)$_2C_6H_3{\cdot}$COEt is hydrogenated (Pd–C in EtOH) to α-hydroxy-α-3 : 4-dimethoxyphenylpropane, b.p. 158—166°/16 mm. (*benzoate*, m.p. 49—50°), also obtained from veratraldehyde and MgEt**I**, and converted by $ZnCl_2$–conc. HCl into (**I**) [*Br*-derivative (**IV**), m.p. 125°]; the change is assumed to depend on an intermediate formation of *iso*eugenol Me ether (**V**). *p*-OMe·$C_6H_4{\cdot}$CHEt·OH is converted by 75% H_2SO_4 into metanethole. Dimerisation of (**V**) by dil. H_2SO_4 or $ZnCl_2$ + HCl or of *cis-iso*eugenol Me ether with MeOH–HCl gives products with m.p. lower than that of (**I**); the m.p. can only be raised to 105° with great loss of material. It is considered that the products are mixtures of stereoisomerides which, however, invariably give (**IV**) when brominated. A stereoisomeride of (**I**) is obtained as follows. The dibromide of (**V**) is converted by Cu-bronze in C_6H_6 at 100° into the bromide of (**I**), which is transformed by Zn powder in boiling 90% EtOH into (**I**), m.p. 105—106°, and by boiling KOH–MeOH into dehydrodi*iso*eugenol Me ether, m.p. 122°. This is hydrogenated (Pd–C in EtOAc) to a *diisoeugenol Me ether*, m.p. 100° (*Br*-derivative, m.p. 110°). H. W.

Diphenylyl hydroxyalkyl ethers.—See B., 1942, II, 361.

Dimethylcarbamate of *m*-hydroxyphenyltrimethylammonium methosulphate (Prostigmin, Proserin). B. R. Bobranski and J. M. Eker (*J. Appl. Chem. Russ.*, 1941, **14**, 524—527).—Nitration of NPhMe_2 affords *m*-$NO_2{\cdot}C_6H_4{\cdot}NMe_2$ (**I**) (65%), which is freed from admixed *p*-isomeride by two fractional pptns. from cold 10% H_2SO_4. (**I**) is reduced (Fe, HCl) to *m*-$NMe_2{\cdot}C_6H_4{\cdot}NH_2$ (80%), converted into *m*-$NMe_2{\cdot}C_6H_4{\cdot}$OH (**II**) (65%) when diazotised in 85% H_2SO_4 (in dil. H_2SO_4 a red dye is formed). *m*-$NMe_2{\cdot}C_6H_4{\cdot}$ONa (prep. by NaOH–EtOH) with a 20% excess of $NMe_2{\cdot}$COCl gives the dimethylcarbamate (57%), b.p. 195°/20 mm., of (**II**). It is converted into the methosulphate (75%), m.p. 143—144°, by Me_2SO_4 in $COMe_2$. G. A. R. K.

Catalytic reduction of *o*- and *iso*-vanillin. F. Mauthner (*J. pr. Chem.*, 1941, [ii], **158**, 321—324).—Hydrogenation of 2 : 3 : 1-OH·C_6H_3(OMe)·CHO in presence of colloidal Pd (not other catalysts) in EtOH gives 2-*hydroxy*-3-*methoxybenzyl* [*o-vanillyl*] *alcohol*, b.p. 162°/12 mm. *iso*Vanillin (p-*nitrophenylhydrazone*, m.p. 203—204°) gives similarly *isovanillyl alcohol*, m.p. 130—131°. Only the acids are isolated after Cannizzaro reactions. R. S. C.

Cationotropic isomerisation of benzyl ether by lithium phenyl. G. Wittig and L. Löhmann (*Annalen*, 1942, **550**, 260—268).—CH_2Ph·OMe with LiPh in Et_2O gives CHPhMe·OH (35%) and a small amount of a hydrocarbon, m.p. 185—186°, reaction involving isomerisation of CHPhLi·OMe to CHPhMe·OLi. Similarly, $(CH_2Ph)_2O$ and LiPh give CH_2Ph·CHPh·OH, m.p. 67—68°. However, CH_2Ph·OEt and LiPh give CH_2Ph·OH (and C_2H_4). The electronic mechanisms of these and similar reactions (Lüttringhaus *et al.*, A., 1939, II, 109) are discussed. R. S. C.

Condensation of *o*-chlorophenol with formaldehyde. F. Hanus (*J. pr. Chem.*, 1941, [ii], **158**, 254—265).—*o*-C_6H_4Cl·OH and 40% aq. CH_2O in 10% NaOH at 40° (24 hr.) and later 20° (48 hr.) give 2-*chloro*-4 : 6-*di*(*hydroxymethyl*)- (**I**), m.p. 117·5—119°, sol. in H_2O, 2-*chloro*-4-*hydroxymethyl*- (**II**), m.p. 123·5—124°, and 2-chloro-6-hydroxymethyl-phenol (**III**). (**II**) is best obtained by interaction for a shorter time. (**III**) is not isolated but its presence is proved by prep. of 2 : 3 : 1-OH·C_6H_3Cl·CHO, m.p. 54·5—55·5° (lit. 54°) (*semicarbazone*, m.p. 240—243°; *oxime*, m.p. 167—168°), from the crude product by oxidation and distillation in steam. The product of Zinke *et al.* (A., 1939, II, 209) was a mixture. With *m*-$NO_2{\cdot}C_6H_4{\cdot}SO_3$Na–NaOH, (**I**) gives 5-*chloro*-4-*hydroxy*i*so*phthalaldehyde, m.p. 127—128° (*dioxime*, m.p. 203—203·5°; *disemicarbazone*, decomp. from 185°), and 3-*chloro*-4(or 2)-*hydroxy*-5-*aldehydobenzoic acid*, m.p. 227·5—228·5° (*semicarbazone*, m.p. 260—263°). Similar oxidation of (**II**) gives 4 : 3 : 1-OH·C_6H_2Cl·CHO, m.p. 127—128° (lit. 129°) (semicarbazone, new m.p. 212°). R. S. C.

Hardening process of phenol–formaldehyde resins. III. F. Hanus [with K. Lercher] (*J. pr. Chem.*, 1941, [ii], **158**, 245—253; cf. A., 1939, II, 476).—Formation of H_2O and CH_2O by graduated heating of 1 : 2 : 4 : 6- (*A*) and 1 : 4 : 2 : 6-OH·C_6H_2X($CH_2{\cdot}$OH)$_2$ (*B*) (X = Me, *cyclo*hexyl, OMe, and Cl) is compared. In all cases the two reactions can be differentiated, the differences being in three cases greater for (*A*). In general the nature of X has less influence in (*A*) than in (*B*). Dialdehydes are formed in all the reactions, but purification is difficult. *α-cyclo*Hexylphenol and 40% aq. CH_2O in 10% NaOH at 15° (3 days) give 2-cyclo*hexyl*-4 : 6-*di*(*hydroxymethyl*)*phenol*, m.p. 104—105°, oxidised by *m*-$NO_2{\cdot}C_6H_4{\cdot}SO_3$Na in boiling 10% NaOH to 4-*hydroxy*-5-cyclo*hexyl*iso*phthalaldehyde*, m.p. 104·5—105·5° (*dioxime*, m.p. 174—175°). Prep. of (*A*) (X = OMe) is improved. R. S. C.

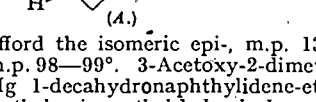
Phenyl *p-cyclo*hexylphenyl sulphone. R. D. Kleene (*J. Amer. Chem Soc.*, 1942, **64**, 1489).—This *substance*, m.p. 108—109·5°, is obtained (50%) by adding $AlCl_3$ to phenyl*cyclo*hexane and $PhSO_2Cl$ in CS_2 and is oxidised by CrO_3 to *p*-$PhSO_2{\cdot}C_6H_4{\cdot}CO_2$H, m.p. 273—274°. R. S. C.

Heterocyclic compounds containing nitrogen. XLIX. Derivatives of *p*-di-β-hydroxyethylbenzene, *m*- and *p*-diacetylbenzene, and *p*-phenylenediacrylic acid. P. Ruggli and W. Theilheimer (*Helv. Chim. Acta*, 1941, **24**, 899—918).—*p*-$C_6H_4(CH_2Br)_2$ (modified prep.) is converted via the dinitrile into *p*-$C_6H_4(CH_2{\cdot}CO_2Et)_2$, vigorous reduction of which with Na–Bu^{α}OH gives 60% of *p*-$C_6H_4(CH_2{\cdot}CH_2{\cdot}OH)_2$ (**I**), m.p. 85—86° [*diacetate* (**II**), m.p. 64—65°; *dibenzoate*, m.p. 136—137°; *di*-p-*nitrobenzoate*, m.p. 172—173°; *bisphenylurethane*, m.p. 212—213°]. (**I**) and conc. HCl or AcOH–HBr at 100° (tube) give p-*di*-β-*chloroethyl*-, m.p. 46—47°, or p-*di*-β-*bromoethyl-benzene* (**III**), m.p. 72—73°, respectively; p-*di*-β-*iodoethylbenzene*, m.p. 110—111°, is prepared from (**III**) and $COMe_2$–NaI. (**III**) and KNO_3–conc. H_2SO_4 at <0° give the 2 : 6-$(NO_2)_2$-derivative (**IV**), m.p. 122—123°, oxidised [HNO_3 (*d* 1·52) at 100° (bath)] to (probably) 2 : 6-*dinitro*-4-*carboxyphenylacetic acid*, decomp. 290—292° (*Me*$_2$ ester, m.p. 142—143°), which could not be decarboxylated satisfactorily [in one case using soda-lime in CO_2 a little (?) *m*-$C_6H_4(NO_2)_2$ was

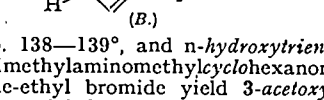
obtained]. 1 : 4 : 2 : 6-$C_6H_2Me_2(NO_2)_2$ is oxidised (CrO_3–conc. H_2SO_4 at <20°) to 2 : 6 : 1 : 4-$(NO_2)_2C_6H_2(CO_2H)_2$ (*Me*$_2$ ester, m.p. 139—141°); *Me*$_2$ 2 : 3- and 2 : 5-*dinitroterephthalate* have m.p. 173—174° and 169—171°, respectively. (**II**) and Ac_2O–HNO_3 (*d* 1·52) followed by 2% MeOH–HCl and then C_5H_5N–BzCl give a *dinitro*-p-*di*-β-*benzoyloxyethylbenzene*, m.p. 157—158°. Reduction ($SnCl_2$, AcOH–HCl) of (**IV**) and treatment of the resulting complex salt with BzCl and 20% NaOH affords 4-*benzamido*-1-*benzoyl*-6-*vinyl*-2 : 3-*dihydroindole*, m.p. 293—294°; the free base resinifies. *m*-$C_6H_4(CHO)_2$ and MgMeBr give *m*-$C_6H_4(CHMe{\cdot}OH)_2$, forms, m.p. 97—98° [*di*-p-*nitrobenzoate*, m.p. 145—148°; *bisphenylurethane* (+C_6H_6), m.p. 103—106° (slight decomp.)] and an oil (*bisphenylurethane*, m.p. 135—137°); both forms are oxidised (CrO_3, aq. AcOH at >20°) to *m*-$C_6H_4(COMe)_2$ (**V**) (*ωω'-Br*$_2$-derivative, m.p. 90—92°). SeO_2 and (**V**) in boiling aq. dioxan give *m*-$C_6H_4(CO{\cdot}CHO)_2$, an oil [amorphous polymeride; *tetra*(*phenylhydrazone*), m.p. 164—165° (decomp.); *diquinoxaline*, m.p. 202—203°, from *o*-$C_6H_4(NH_2)_2$]. The *dipyridinium* salt of *p*-$C_6H_4(CO{\cdot}CH_2Br)_2$ with *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ in aq. EtOH–NaOH at ~0° affords the *nitrone*, *p*-$C_6H_4(CO{\cdot}CH{:}NO{\cdot}C_6H_4{\cdot}NMe_2$-*p*)$_2$, decomp. 132—134°, hydrolysed (2N-EtOH–HCl in dioxan) to *p*-$C_6H_4(CO{\cdot}CHO)_2$. *p*-$C_6H_4(CHO)_2$, $CH_2(CO_2H)_2$, and C_5H_5N–piperidine at 45—50° and later at 100° (bath) give *p*-$C_6H_4(CH{:}CH{\cdot}CO_2H)_2$ (82%), decomp. >360° [*dichloride* (**VI**) (prep. by $SOCl_2$), m.p. 170—171°; *diamide*, m.p. 320° (decomp.); *dianilide*, m.p. 292—294°; *di*-p-*toluidide*, m.p. 331—334°], the *dihydrazide*, m.p. 258—260° (decomp.), of which with HNO_2 yields p-*phenylene*-5 : 5'-*di*-(1-*nitroso*-3-*pyrazolidone*). Activated NaN_3 and (**VI**) in C_6H_6 afford the diazide, decomp. 100—105°, which in boiling C_6H_6 followed by MeOH gives the *urethane*, *p*-$C_6H_4(CH{:}CH{\cdot}NH{\cdot}CO_2Me)_2$, decomp. >360°. H. B.

Interaction of amines with nitrous acid. W. Hückel and E. Wilip (*J. pr. Chem.*, 1941, [ii], **158**, 21—32).—*cyclo*Hexylamine (~0·5) and $NaNO_2$ (~0·58) in AcOH (0·58 mol.) + H_2O (17·5 mols.) give *cyclo*hexanol (**I**), *cyclo*hexene (**II**), and *cyclo*hexyl acetate (**III**). Replacement of the H_2O by 5% aq. EtOH gives *cyclo*hexyl Et ether (**IV**) and (**I**) in the ratio 5 : 1 and by 25% aq. EtOH in the ratio 1 : 1, (**IV**) being formed at the expense of (**I**) and the amount of (**II**) being unchanged; further increase in the [EtOH] has little effect on the ratio. No reaction occurs in EtOH or MeOH. In 3·3 and 33·3 mol.-% AcOH the ratio of (**I**) to (**III**) obtained is 20 : 1 and 2·5 : 1, respectively, but (**III**) is formed at the expense of (**II**). *l*-Menthylamine and HNO_2 in H_2O give pure *l*-menthol, but in aq. EtOH inversion occurs leading to *l*-menthyl and *d*-neomenthyl Et ethers. *trans*-Carvomenthylamine-I (=*l*-neocarvomenthylamine) gives much carvomenthone-II and a little -I with 4 : 1 Δ^1- + *trans*-Δ^2-menthene. *l*-Carvomenthone and *l*-menthene thus belong to sterically different series. Reaction mechanisms are discussed. R. S. C.

Attempted synthetic preparation of the antirachitic vitamin. VIII. Model substances with a hydroxyl group in ring A. K. Dimroth and E. Stockstrom (*Ber.*, 1942, **75**, [*B*], 510—521).—α-3-Acetoxy-6-dimethylaminomethyl*cyclo*hexanone is converted by Mg 1-decahydronaphthylidene-ethyl bromide into α-n-3-*acetoxy*-6-*dimethylaminomethyl*-1-*decahydronaphthylidene-ethyl*cyclo*hexanol* (**I**), m.p. 188·5°, and the corresponding α-epi-*derivative* (**II**), m.p. 135°. The β-n-*compound* (**III**), m.p. 147—149°, is obtained similarly from β-3-acetoxy-6-dimethylaminomethyl*cyclo*hexanone. Successive treatment of (**II**) in C_6H_6 with PBr_3 and powdered KOH gives the absorbing α-epi-3-*hydroxy*-6-*dimethylaminomethyl*cyclo*hexylidene*-β-1-*decahydronaphthylidene-ethane* (**IV**), m.p. 176—178°, and the non-absorbing epi-3-*hydroxy*-6-*dimethylaminomethyl*-1-*decahydronaphthylidene-ethyl*-Δ^1-cyclo*hexene* (**V**), m.p. 156—157°. Similarly (**I**) affords the absorbing α-n-3-*hydroxy*-6-*dimethylaminomethyl*cyclo*hexylidene*-β-1-*decahydronaphthylidene-ethane* (**VI**), m.p. 140—141°, and n-3-*hydroxy*-6-*dimethylaminomethyl*-1-*decahydronaphthylidene-ethyl*-Δ^1-cyclo*hexene* (**VII**), m.p. 103—104°. (**III**) gives β-n-3-*hydroxy*-6-*dimethylaminomethyl*cyclo*hexylidene*-β-1-*decahydronaphthylidene-ethane* (**VIII**), m.p. 95—97°, and (**VII**). Hofmann degradation of (**IV**) gives the epi*hydroxytriene* (*A*), m.p. 80—81°, whereas (**VI**) and (**VIII**) yield the n-*hydroxytriene* (*A*), m.p. 102°, and (**V**) and (**VII**)



(*A.*)



(*B.*)

R = $C_{10}H_{16}$

afford the isomeric epi-, m.p. 138—139°, and n-*hydroxytriene* (*B*), m.p. 98—99°. 3-Acetoxy-2-dimethylaminomethyl*cyclo*hexanone and Mg 1-decahydronaphthylidene-ethyl bromide yield 3-*acetoxy*-2-*dimethylaminomethyl*-1-*decahydronaphthylidene-ethyl*cyclo*hexanol*, m.p. 108—109°, dehydrated to the absorbing α-3-*hydroxy*-2-*dimethylaminomethyl*cyclo*hexylidene*-β-1-*decahydronaphthylidene-ethane*, m.p. 165—166°. H. W.

Steric promotions and inhibitions of polarisations. G. Baddeley (*Nature*, 1942, **150**, 178—179; cf. A., 1940, I, 11; *Ann. Rep. C.S.*, 1941, **38**, 127).—The data of Klcene *et al.* (A., 1941, I, 264) offer an example (*loc. cit.*) that polarisation can be promoted as well as hindered by steric congestion. In *cis*-cinnamic acid (**I**) the orient ation of the CO_2H is unfavourable to the development of a greater electron density in its vicinity so that (**I**) is more ionised than the *trans*-isomeride. In *cis*-2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CH{:}CH{\cdot}CO_2H$ the CO_2H is in the same plane as the C atoms embracing the double linking so that the dissociation const. is < that of the *trans*-isomeride. 1-Keto-5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (**II**) is converted by $AlCl_3$ into the 5 : 7-isomeride and hydrolysed (H_3PO_4) to γ-2 : 5-dimethylphenylbutyric acid, but 4 : 7-dimethyl-α-hydrindone cannot react similarly. In (**II**) ring puckering can allow steric conditions to inhibit the mesomeric effect of the CO. An explanation of the lower reactivity (towards deuteration) of carbazole derivatives relative to those of $NHPh_2$ is given. W. C. J. R.

Restricted rotation of *o*-substituted styrene derivatives. G. Wittig, A. Oppermann, and K. Faber (*J. pr. Chem.*, 1941, [ii], **158**, 61—71).—3 : 5 : 1-$C_6H_3Me_2{\cdot}OBz$ and $AlCl_3$ at room temp. and then 140° give 4-*benzoyl*-m-5-*xylenol* (55%), m.p. 139—140°, converted by $(CH_2Ph{\cdot}CO)_2O$–$CH_2Ph{\cdot}CO_2Na$ at 210° into 3 : 4-*diphenyl*-5 : 7-*dimethylcoumarin* (69%), m.p. 169—170°, which with, successively, boiling NaOH–MeOH, Me_2SO_4–H_2O, and boiling NaOH–aq. MeOH gives 2-*methoxy*-αβ-*diphenyl*-4 : 6-*dimethylcinnamic acid* (73%), m.p. 203—204°. The K salt thereof with $Cl{\cdot}[CH_2]_2{\cdot}NMe_2$ in dioxan at 120° gives the β-*dimethylaminoethyl* ester (80%), m.p. 80—82° (picrate, m.p. 169·5—170·5°), which yields the d-*ester*, m.p. (preheated at 78°) 78·3—83·0°, $[\alpha]_D^{20}$ +39·0° in MeOH, half-life period 43 min. at 20°, by way of the (+)-α-*bromocamphor*-β-*sulphonate*, $[\alpha]_D^{20}$ +75·9° → +42·2° in 4 hr. in MeOH. R. S. C.

Kolbe electrochemical syntheses with aromatic acids. F. Fichter and K. Kestenholz (*Helv. Chim. Acta*, 1942, **25**, 785—792).—Electrolysis of $CHPh{:}CH{\cdot}[CH_2]_2{\cdot}CO_2H$, partly neutralised with KOH, in MeOH–C_5H_5N gives the Me ester, δ-*phenyl*-Δ$^\gamma$-*buten*-α-*ol*, b.p. 99—101°/12 mm. (p-*nitrobenzoate*, m.p. 119°), and, by loss of CO_2 and cyclisation, a small amount of a saturated *hydrocarbon*, $C_{20}H_{22}$, m.p. 89—90°. *o*-, *m*-, and *p*-$C_6H_4Me{\cdot}O{\cdot}CH_2{\cdot}CO_2H$ give αβ-di-*o*-, m.p. 85—86° (lit. 79°), b.p. 184—186°/12 mm. [$(NO_2)_4$-derivative, m.p. 159·5—160·5°] (with some ? *o*-$C_6H_4Me{\cdot}OMe$), -*m*-, m.p. 96·5—97°, b.p. 192—195°/12 mm. [$(NO_2)_5$-derivative, m.p. 165·5—166°], and -*p*-tolyloxyethane, m.p. 133·5°, b.p. 200—202°/12 mm. R. S. C.

Decomposition of benzoyl peroxide in benzene.—See A., 1942, I, 370.

β-Alkylaminoethyl *p*-aminobenzoates.—See B., 1942, III, 223.

Applications of the bromometric assay. I. Bromination of derivatives of aminobenzoic acids. E. H. Wells (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 537—546).—Except for monocaine and amylcaine, results obtained by the indirect method agree with those obtained by the direct method. The following appear new or revised: Me, m.p. 131—132·5° (lit. 127—128°); *Pr*, m.p. 81·8—83°; *Bu*$^\alpha$, m.p. 62—64·4°; *Bu*$^\beta$, m.p. 74—75°; γ-diethylamino-ββ-dimethylpropyl [*hydrobromide*, m.p. 172—174° (decomp.); *hydrochloride*, m.p. 165—166·5° (decomp.)]; β-diethylamino-δ-methyl-*n*-amyl [*hydrobromide*, m.p. 192—195° (decomp.); *hydrochloride*, m.p. 163—168° (decomp.)]; γ-dimethylamino-αβ-dimethylpropyl [*hydrobromide*, m.p. 246—247° (decomp.); *hydrochloride*, m.p. 223—228° (decomp.) (softens 203—206°)]; β-*iso*butylaminoethyl [*hydrobromide*, m.p. 204—206° (decomp.); *hydrochloride*, m.p. 209—211° (decomp.)]; β-*n*-amylaminoethyl [*hydrobromide*, m.p. 195·8—197° (decomp.); *hydrochloride*, m.p. 205·5—207° (decomp.)]; β-diethylaminoethyl [hydrobromide, m.p. 236—237·5° (decomp.) (lit. 217°); *hydrochloride*, m.p. 234—236° (decomp.)]; γ-dibutylamino-*n*-propyl [*hydrochloride*, m.p. 143·6—146° (decomp.)] 3 : 5-dibromo-4-aminobenzoate; *Me* m-*aminobenzoate hydrochloride*, m.p. 202—205° (decomp.). A. A. E.

Isomerism of disalicylides. I. Disalicylic anhydride and its conversion into α- and β-disalicylide. L. Anschütz and R. Neher (*J. pr. Chem.*, 1941, [ii], **159**, 264—272).—Repetition of previous work (A., 1922, i, 456) on the elimination of H_2O from disalicylic acid (**I**) shows that neither α- (**II**) nor β-disalicylide (**III**) can have the structure of *disalicylic anhydride* (**IV**), but are probably *cis*- and *trans*-forms. (**IV**), m.p. 248—250°, obtained with a little xanthone-4-carboxylic acid from (**I**) and boiling Ac_2O or cold C_6H_6–C_5H_5N–$SOCl_2$, with aq. alkali affords (**I**) and when distilled at 14 mm. gives (**II**) and (**III**). (Cf. A., 1942, II, 312.) C. S.

Polyhydroxy-3-aminomethylphthalides.—See B., 1942, III, 223.

Action of hydrazoic acid on phthalic anhydride in presence of concentrated sulphuric acid. G. Caronna (*Gazzetta*, 1941, **71**, 189—194).—*o*-$C_6H_4(CO)_2O$ in conc. H_2SO_4 with NaN_3 at 40—50° gives isatoic acid, *o*-$C_6H_4(NH)_2CO$, and *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ (the sole product at >110°). E. W. W.

Luminescence of luminol.—See A., 1942, I, 352.

Formation and structure of diphthalylbenzidine and related compounds. G. Wanag and A. Veinbergs (*Ber.*, 1942, **75**, [*B*], 725—736).—Diphthalylbenzidine (**I**) is formed when dil. solutions of *o*-$C_6H_4(CO)_2O$ (**II**) and ($C_6H_4{\cdot}NH_2$-*p*)$_2$ in AcOH are mixed and boiled, whereas 4 : 4'-diphenylenediphthalamic acid (**III**), m.p. 382—384° after becoming yellow at 200—220° (Na_2 and K_2 salts), separates immediately from the cold, more conc. solution of the reactants.

(III) and boiling PhCHO yield *dibenzylidenebenzidine*, m.p. 235—245°, reconverted into (I) by (II) in AcOH. (III) and boiling Ac_2O afford *N'*-phthalyl-*N*-acetylbenzidine and (I). (I) is transformed into (III) by NaOMe. The yellow colour of (I) is assumed to be due to its production from the *iso* form ·N:C·O·C:O and not ·CO·N·CO·. *o*-Tolidine (IV) and (II) in AcOH at room temp. give 3 : 3'-*dimethyl*-4 : 4'-*diphenylenediphthalamic acid*, m.p. 328° (becoming yellow) (K_2 salt), converted by boiling Ac_2O into *diphthalyl*-*o*-*tolidine*, yellow, m.p. 248—250°, and colourless (stable) form, m.p. 332°, also obtained from (IV) and (II) in boiling AcOH. *o*-Anisidine similarly affords 3 : 3'-*dimethoxy*-4 : 4'-*diphenylenephthalamic acid*, m.p. 354—356° (Na_2 salt), or *diphthalyl*-*o*-*anisidine*, m.p. 359° (darkening). $CH_2(C_6H_4\cdot NH_2\text{-}p)_2$ and (II) in AcOH at ~30° give (after dilution with H_2O) *diphenylmethane*-4 : 4'-*diphthalamic acid*, m.p. 132° (with evolution of H_2O and resolidification); *o*- and *p*-$C_6H_4(NH_2)_2$ similarly afford *o*-, m.p. 183° (loss of H_2O), and p-*phenylenediphthalamic acid*, m.p. 358°, respectively. p-*Diphenylyl*-, m.p. 272°, α-, m.p. 189° (loss of H_2O), and β-*naphthyl*-, m.p. 216° (loss of H_2O), and *phenyl*-*phthalamic acid*, m.p. 164° (loss of H_2O), are readily obtained from NH_2Ar and (II) in AcOH at ~30°. H. W.

Sterio structure of benzylideneaniline. C. Wiegand and E. Merkel (*Annalen*, 1942, **550**, 175—181).—Absorption spectra of *trans*-(CHPh:)$_2$ (I) and 2-phenylindene (II) (in dioxan) are very similar. Replacement of $C_{(1)}$ and $C_{(3)}$ of (II) by N or NH has little effect, so that the absorption of (II) closely resembles that of 2-phenylbenziminazole. That of CHPh:NPh (III) is markedly different. Mixed m.p. diagrams of (III) with (I), *trans*-(NPh:)$_2$, $(CH_2Ph)_2$, and phenanthridine are of type III (Rheinboldt *et al.*, A., 1926, 908); (I) and $(CH_2Ph)_2$ form perfect mixed crystals; (I) and phenanthrene give a simple eutectic. Thus, (III) has not the *trans* structure; since the *cis* structure is excluded by dipole moments, it is probable that the NPh of (III) has linear alignment (cf. de Gaouck *et al.*, A., 1938, II, 280). R. S. C.

Pyrogenic oxido-reduction of benzylidene-*o*-phenylenediamine.—See A., 1942, II, 380.

Application of the method of von Fedorov's crystallo-chemical analysis to derivatives of β-resorcylaldehyde. M. Seshaiyengar (*J. Mysore Univ.*, 1942, **B, 3**, 51—54).—The optical properties of a no. of derivatives of β-resorcylaldehyde are tabulated. The identity of, *e.g.*, 3 : 2 : 4 : 6 : 1-OMe·$C_6HBr_2(NO_2)$·OH [obtained by bromination of 4 : 5 : 2 : 1-OMe·$C_6H_2(NO_2)$(OH)·CHO and 3 : 6 : 1-OMe·$C_6H_3(NO_2)$·OH and by nitration of 4 : 3 : 5 : 2 :1-OMe·C_6HBr_2(OH)·CHO] is thereby proved. A. J. M.

Liquid-crystalline substances with side-chains of the type, OR·[CH$_2$]$_n$·O. C. Weygand, R. Gabler, and N. Bircan (*J. pr. Chem.*, 1941, [ii], **158**, 266—274).—When the Alk of *p*-OAlk·C_6H_4·N:N(O)·C_6H_4·OAlk-*p* are replaced by OAlk·CH_2·O, the liquid-cryst. properties are depressed or repressed. Claims of G.P. 209,608 are incorrect, but *p*-NO_2·C_6H_4·OK (I) with CH_2Cl·OR in $COMe_2$ at 0° gives *p*-methoxy- (II), m.p. 24—25°, b.p. 166—167°/14 mm., and p-*butoxy*-*methoxynitrobenzene*, m.p. 13·5°, b.p. 159°/5·5 mm. *CH_2Cl Bu^{a}ether*, b.p. 36°/14 mm., is obtained (90%) from Bu^{a}OH by paraformaldehyde–HCl. *p*-CHO·C_6H_4·OK (III) gives similarly *p*-methoxy- (61%), b.p. 139°/11 mm., and p-*ethoxymethoxybenzaldehyde* (70%), b.p. 128—129°/7 mm. $FeSO_4$–NH_3–MeOH–H_2O reduces (II) to p-*methoxymethoxyaniline* (71%), b.p. 138—139°/11 mm. OMe·[CH_2]$_2$·Br with EtOH and (I) at 150° or (III) at 160—170° gives p-β-*methoxyethoxy*-*nitrobenzene* (64%), m.p. 84°, or *-benzaldehyde* (50%), an oil, respectively. Electrolytic reduction of the NO_2-compound in NaOAc–EtOH gives 4 : 4'-*dimethoxy*- (45%), m.p. 109°, and *-dibutoxy*-*methoxyazoxybenzene* (50%), m.p. 31°, but 4 : 4'-*di*-β-*methoxyethoxyazobenzene* (49%), m.p. 135°. NH_2R, and R'CHO in boiling EtOH give p-*methoxymethoxybenzylidene*-p'-*methoxymethoxy*-*aniline*, m.p. 47°, and -p'-*phenetidine*, m.p. 80·5°, p-*ethoxymethoxybenzylidene*-p'-*phenetidine*, m.p. 64°, *Et* p-*methoxymethoxy*-, m.p. 54° (*Bz*-I, 79°, and *Bz*-II form, 76°), and p-β-*methoxyethoxy*-*benzylidene*-p'-*aminocinnamate*, m.p. 65° (*Bz*-I, 154°, and *Bz*-II form, unsharp), p-β-*methoxyethoxybenzylidene*-p'-*phenetidine*, m.p. 109°, 4-p-n-*propoxy*-, m.p. 107° (*Pl*-form, 227°), and 4-p-*methoxymethoxy*-*benzylideneamino*-1-p-*methoxybenzeneazonaphthalene*, m.p. 118° (*Pl*-form, 189°). R. S. C.

Nitrones. II. Condensation of aryl nitroso-compounds with dinitrotoluene. I. Tănăsescu and I. Nanu (*Ber.*, 1942, **75**, [*B*], 650—655; cf. A., 1939, II, 323).—1 : 2 : 4-$C_6H_3Me(NO_2)_2$ and *o*-C_6H_4Me·NO in boiling 96% EtOH in presence of piperidine give 2 : 4-dinitrobenzylidene-*o*-toluidine (I), m.p. 153°, whereas in presence of Na_2CO_3 or Na_2HPO_4 the product is 2 : 4-*dinitrobenz*-*o*-*toluidide* (II), m.p. 227°, with a small amount of (I). The constitution of (II) is established by the dark violet colour which it gives with conc. H_2SO_4 and a little $K_2Cr_2O_7$, by its synthesis from 2 : 4 : 1-$(NO_2)_2C_6H_3$·COCl and *o*-C_6H_4Me·NH_2 in boiling C_6H_6, and from the formation of a N-*Ac* derivative (III), m.p. 218°. Addition of KOH–MeOH to a solution of *o*-C_6H_4Me·NO and 2 : 4 : 1-$(NO_2)_2C_6H_3$·CH_2Cl in EtOH at >15° affords 2 : 4-*dinitrophenyl*-N-*o*-*tolylnitrone*, m.p. 99·5°, isomerised to (II) by boiling KOH–EtOH or by AcCl in boiling $COMe_2$, and converted into (III) by NaOAc and Ac_2O at 100°. 1 : 2 : 4-$C_6H_3Me(NO_2)_2$ and *m*-C_6H_4Me·NO in boiling 96% EtOH containing Na_2CO_3 give a mixture of 2 : 4-*dinitrobenz*-m-*toluidide* (IV), m.p. 178° [also obtained from 2 : 4 : 1-$(NO_2)_2C_6H_3$·COCl and *m*-C_6H_4Me·NH_2], and 2 : 4-*dinitrophenyl*-N-m-*tolylnitrone* (V), m.p. 161°, obtained exclusively when piperidine is used as condensing agent. (V) is isomerised to (IV) by AcCl in boiling $COMe_2$. 2 : 4-*Dinitrobenz*-N-*acet*-m-*toluidide*, m.p. 158·5°, is obtained from (IV), (V), Ac_2O, and anhyd. NaOAc at 100°. H. W.

Application of the Friedel–Crafts reaction to (A) methoxy-, (B) *o*-alkoxy-diphenyl ethers. M. Tomita (*J. Pharm. Soc. Japan*, 1934, **54**, 897—904; 1936, **56**, 492—497).—(A) *o*-Methoxy- and 2 : 2'-dimethoxy-diphenyl ether, AcCl, and $AlCl_3$ yield 5 : 4'- or 5 : 5'-(not 4 : 4'-)Ac_2 derivatives. 5 : 4'-*Diacetyl*-, m.p. 142° [*semicarbazone*, m.p. 239° (decomp.)], and 5 : 4'-*bischloroacetyl*-, m.p. 148°, -2-*methoxydiphenyl ethers* yield 5 : 4'-*dicarboxy*-2-*methoxydiphenyl ether*, m.p. 310°, on oxidation. Similarly 2 : 2'-*dimethoxy*-5 : 5'-*bischloroacetyldiphenyl ether*, m.p. 154—155°, yields 5 : 5'-*dicarboxy*-2 : 2'-*dimethoxydiphenyl ether*, m.p. 295°; the isomeric 4 : 4'-*dicarboxylic acid*, m.p. 255°, is obtained by condensing Me vanillate with 3 : 4 : 1-OMe·C_6H_3Br·CO_2Me. (B) *o*-OH·C_6H_4·OPh, PrI, and MeOH–NaOMe at 120—130° (bath) yield o-*propoxydiphenyl ether*, m.p. 128—129°, which with AcCl and $AlCl_3$ in CS_2 gives 2-*propoxy*-5 : 4'-*diacetyldiphenyl ether*, m.p. 99° (*semicarbazone*, m.p. 205°), oxidised to 5 : 4'-*dicarboxy*-2-*propoxydiphenyl ether*, m.p. 237°. o-iso*Amyloxydiphenyl ether*, b.p. 145—146°/3 mm., 2-iso*amyloxy*-5 : 4'-*diacetyldiphenyl ether*, m.p. 56—59° [*semicarbazone*, m.p. 192° (decomp.)], and 5 : 4'-*dicarboxy*-2-iso*amyloxydiphenyl ether*, m.p. 230—231°, were similarly obtained. CH. ABS. (*c*)

Constitution of kynurenine. A. Butenandt, W. Weidel, and W. von Derjugin (*Naturwiss.*, 1942, **30**, 51).—Kynurenine (I), $C_{10}H_{12}O_3N_2$, is a monocarboxylic acid. Its ultra-violet absorption spectrum resembles that of *o*-NH_2·C_6H_4·COMe, into which it is converted by alkali. *o*-NO_2·C_6H_4·CO·CH_2Br is condensed with *o*-$C_6H_4(CO)_2N$·$CNa(CO_2Et)_2$ to *Et$_2$ phthalimido*-o-*nitrophenacylmalonate*, m.p. 155—156°, transformed by energetic acid hydrolysis into α-amino-α-keto-γ-*o*-nitrophenylbutyric acid (*hydrochloride*, m.p. 186—187°). This is reduced to the $(NH_2)_2$-derivative, characterised as the sulphate, m.p. 194° (decomp.), darkens at 166°, identical apart from its racemic character with the sulphate of natural (I). (I) is therefore l-α-*amino*-γ-*keto*-γ-o-*aminophenylbutyric acid*. H. W.

Derivatives of benzoin and deoxybenzoin hydrogenated in one nucleus. P. Ruggli and A. Businger (*Helv. Chim. Acta*, 1941, **24**, 1112—1126).—PhOMe, *cyclo*hexylacetyl chloride, and $AlCl_3$ in CS_2 afford p-*anisyl hexahydrobenzyl ketone* (I), m.p. 43—44° (*oxime*, m.p. 97—98°; *semicarbazone*, m.p. 166—167°; 2 : 4-*dinitrophenylhydrazone*, m.p. 193—195°), and an unidentified substance, m.p. 140—141°. Similarly PhOMe, 4-methoxy*cyclo*hexylacetyl chloride, and $AlCl_3$ yield p-*anisyl* p-*methoxyhexahydrobenzyl ketone* (probably trans-) [*hexahydrodeoxyanisoin*] (II), m.p. 69—70° (*semicarbazone*, m.p. 172—173°; 2 : 4-*dinitrophenylhydrazone*, m.p. 175—177°), accompanied by much non-cryst. product containing probably the *cis*-derivative and certainly (I); condensation is better effected by $SnCl_4$ in C_6H_6. Treatment of (II) with NaOEt or $NaNH_2$ followed by EtI gives an *O*-Et compound. Gradual addition of α-4-methoxy*cyclo*hexyl-*n*-butyryl chloride to PhOMe and $SnCl_4$ in C_6H_6 affords β-4-*methoxycyclohexyl*-2-p-*anisylbutan*-α-*one* [α-*ethylhexahydrodeoxyanisoin*] (III), b.p. 150—160°/12 mm. (which does not give a cryst. oxime, semicarbazone, or dinitrophenylhydrazone), with an unidentified liquid, b.p. 75—85°/12 mm. (III) and MgEtI yield δ-4-*methoxy*cyclo*hexyl*-γ-p-*anisylhexan*-γ-*ol*, from which H_2O could not be satisfactorily withdrawn by PBr_3 under varied conditions. Propionoin (IV) and *p*-OMe·C_6H_4·MgBr give γ-*p*-anisylhexane-γδ-diol, m.p. 180—181°, converted by distillation under atm. pressure or by boiling with 50% H_2SO_4 into δ-*p*-anisylhexan-γ-one; this with MgMeI affords δ-*p*-anisyl-γ-methylhexan-γ-ol (p-*nitrobenzoate*, m.p. ~180°). γ-cyclo*Hexylhexane*-γδ-*diol*, m.p. 77—78°, from (IV) and Mg *cyclo*hexyl bromide (V), is converted by boiling 25% H_2SO_4 into δ-*cyclo*hexylhexan-γ-one (2 : 4-*dinitrophenylhydrazone*, m.p. 179—181°). *p*-OMe·C_6H_4·CH(OH)·CN (VI) and (V) give β-*keto*-β-cyclo*hexyl*-α-p-*anisylethyl alcohol*, m.p. 72—73°, from which β-cyclo*hexyl*-α-p-*anisylbutane*-αβ-*diol*, m.p. 91—93°, is obtained by MgEtBr; this is converted by boiling 50% H_2SO_4 into β-cyclo*hexyl*-α-p-*anisylbutan*-α-*one* (2 : 4-*dinitrophenylhydrazone*, m.p. 200—201°), which reacts only incompletely with MgEtBr and does not appear to give an unsaturated stilbene derivative. (VI) and Mg *cyclo*pentyl bromide give β-*keto*-β-cyclo*pentyl*-α-p-*anisylethyl alcohol*, m.p. 70—71°. H. W.

4 : 4'-Diaminobenzophenone and other sulphur-free compounds with sulphonamide activity. R. Kuhn, E. F. Möller, G. Wendt, and H. Beinert (*Ber.*, 1942, **75**, [*B*], 711—719).—Every alteration effected in the mol. of *p*-NH_2·C_6H_4·CO_2H (I) has depressed or nullified its great growth-promoting activity. Among derivatives of (I) there are several which are free from S and have a restrictive action resembling that of the sulphonamides; the restriction is countered by (I). Bu, m.p. 56—57°, lauryl, m.p. 81—83°, and cetyl, m.p. 86—87°, *p*-aminobenzoate have no bacteriostatic pro-

perties (the corresponding *p*-NO_2-esters have m.p. 34—35°, 43—44°, and 53—55°, respectively); this is true also of *cis*- and *trans*-4-amino- and *cis*- and *trans*-4-hydroxy-hexahydrobenzoic acid. *p*-$NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$ is inactive. *p*-$NH_2{\cdot}C_6H_4{\cdot}CS{\cdot}NH_2$ greatly diminishes the rate of growth of *Streptobacterium plantarum*, but this is not a "sulphonamide" action, since it is not countered by (I). 2-p-*Aminobenzamidopyridine* ("*carbopyridine*"), m.p. 168° (*dihydrochloride*), has a similar but much weaker action than sulphapyridine. *p*-$NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$, *p*-*p'*-aminobenzamidobenzoic acid (*Me* ester, m.p. 235°; *Me* ester, m.p. 244°, of the *p'*-NO_2-acid), and *Me* p'-*nitrobenzoyl*-p-p'-*aminobenzamidobenzoate*, m.p. 365° (decomp.), are essentially inactive. $CO(C_6H_4{\cdot}NH_2\text{-}p)_2$ (*dihydrochloride*, softens and darkens at 250°) like $SO_2(C_6H_4{\cdot}NH_2\text{-}p)_2$ has a sp. "sulphonamide" action which is cancelled by (I). *p*-$NO_2{\cdot}C_6H_4{\cdot}COMe$ is more active than *p*-$NH_2{\cdot}C_6H_4{\cdot}COMe$. *p*-$NH_2{\cdot}C_6H_4{\cdot}PO(OH)_2$ but not $NHAc{\cdot}C_6H_4{\cdot}PO(OH)_2$ has "sulphonamide" action. The toxicity of $CO(C_6H_4{\cdot}NH_2\text{-}p)_2$ towards mice is not countered by (I). 4-*Methyl*-5-p-*nitrobenzoyloxyethylthiazole*, m.p. 123°, and the corresponding NH_2-derivative, m.p. 126—127°, are described. H. W.

γ-Diketones. II. ***cyclo*Pentenone ring closure of γ-diketones, $COMe{\cdot}[CH_2]_2{\cdot}CO{\cdot}CH_2R$.** H. Hunsdiecker (*Ber.*, 1942, **75**, [*B*], 455—460).—Ring closure of $COMe{\cdot}[CH_2]_2{\cdot}CO{\cdot}CH_2R$ to *cyclo*pentenones with intact Me occurs in presence of aq. alkalis, alcoholic alkali alkoxide, readily hydrolysable salts, org. bases such as piperidine, or of borax or NaOAc solutions at higher temp. The yields are 80—95%. With α-acyl-lævulates ketone fission precedes cyclisation under these conditions, but if abs. MeOH–NaOMe in presence of EtOAc is used CO_2Et is wholly or largely retained. The following 2-substituted 3-*methyl*-Δ^2-*cyclopentenones* have been obtained and the m.p. of the corresponding *semicarbazones* are recorded in parentheses: 2-*methyl*-, b.p. 75°/16 mm. [247° (decomp.)]; 2-*propyl*-, b.p. 94·5°/11·5 mm., (212°); 2-butyl- b.p. 107°/12 mm. (193°); 2-amyl-, b.p. 120°/12 mm. (176°); 2-iso*amyl*-, b.p. 114·5°/12 mm. (181·5°); 2-hexyl-, b.p. 144°/18 mm. (164°); 2-*octyl*-, b.p. 157°/12 mm. (159°); 2-*dodecyl*-, b.p. 171°/2·5 mm., m.p. 34° (152°); 2-ε-*methoxyamyl*-, b.p. 145°/14 mm. (151°); 2-γ-iso*amyloxy*-n-*butyl*-, b.p. 132°/3 mm. (131°); 2-*carboxymethyl*-, m.p. 108·5—110·5° (215°); 2-ε-*carboxyamyl*-, b.p. 182°/2 mm., m.p. 63°, and its *Me* ester, b.p. 136°/1 mm.; 4-*methyl*-2-*butyl*-, b.p. 115°/14 mm. [232° (decomp.)]; 5-*methyl*-2-*butyl*-, b.p. 104°/11 mm.; 4-*methyl*-2-iso*propyl*-, b.p. 78°/2·5 mm.; 5-*carbomethoxy*-4-*methyl*-2-iso*propyl*-, b.p. 93°/3 mm.; 5-*carbomethoxy*-2-*butyl*-, b.p. 130°/5 mm. H. W.

γ-Diketones. III. Synthesis of jasmone. H. Hunsdiecker (*Ber.*, 1942, **75**, [*B*], 460—468).—2-Methyl-5-γ-ketohexylfuran is reduced [$Al(OPr^\beta)_3$ in $Pr^\beta OH$] to the *sec.*-alcohol, b.p. 102—109°/3 mm., dehydrated by H_3PO_4-active C at 260—270° to a mixture of 2-methyl-5-hexenylfurans. Boiling aq. AcOH–H_2SO_4 transforms this into a mixture of undecene-βε-diones which when boiled with 2% KOH affords jasmone [3-methyl-2-Δ^β-pentenyl-Δ^2-*cyclo*pentenone] (I) in poor yield. Δ^γ-Hexenol, from oil of peppermint, is converted by PBr_3 and C_5H_5N into α-bromo-Δ^γ-hexene (II), b.p. 51—57°/17 mm., with, apparently, a *bromohexanol*, b.p. 100—102°/15 mm. (II) is transformed through the nitrile, b.p. 78—80°/15 mm., into Δ^γ-*heptenoic acid* (III), b.p. 104—109°/5 mm., the chloride, b.p. 66·5°/14 mm., of which with $CHNaAc{\cdot}CO_2Et$ affords Et heptenoylacetoacetate (corresponding Me ester), the Na derivative of which is converted by $COMe{\cdot}CH_2Br$ into Et α-heptenoyllævulate. This and hot 3% NaOH yield (I). *iso*Amyl β-*iso*amyloxybutyrate, b.p. 130—134°/13 mm., is hydrolysed to the *acid*, b.p. 134—139°/12·5 mm., which when co-electrolysed with $Ac{\cdot}[CH_2]_2{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H$ gives αε-di*iso*amyloxyhexane, b.p. 115—124°/5 mm., tetradecanetetraone, m.p. 102—103°, and ι-*iso*amyloxydecane-βε-dione (IV), b.p. 139°/2 mm. (IV) is unchanged or resinified by HBr or dil. mineral acids, thus giving little promise of the prep. of (I) along these lines.

[With E. Wirth.] $CH_2{:}CH{\cdot}CHO$ and MgEtBr afford $CH_2{:}CH{\cdot}CHEt{\cdot}OH$, whence successively $CH_2Br{\cdot}CH{:}CHEt$, (III), and (I). Attempts to obtain (III) from $Me{\cdot}[CH{:}CH]_2{\cdot}CHO$ or $Me{\cdot}[CH{:}CH]_2{\cdot}CH_2{\cdot}OH$ are less satisfactory. (I) is probably a *trans* form. H. W.

Photochemical reactions between ketones and alcohols. A. Banchetti (*Gazzetta*, 1941, **71**, 163—171).—$COPh_2$ (I) and *cyclo*hexanol in C_6H_6 irradiated with ultra-violet light give $(CPh_2{\cdot}OH)_2$ (II) and *cyclo*hexanone. (I) and *trans*-decahydro-β-naphthol in C_6H_6 in sunlight or ultra-violet light give (II) and *trans*-β-ketodecahydronaphthalene, with unidentified *products*, including $(C_7H_7O)_x$ (?). β-$C_{10}H_7{\cdot}COMe$ and $CH_2Ph{\cdot}CO_2H$ or AcOH in C_6H_6 in sunlight give no significant reaction. E. W. W.

Cyclitols. V. Inosose obtained biochemically. T. Posternak (*Helv. Chim. Acta*, 1941, **24**, 1045—1058).—The inosose (I) obtained from conc. HNO_3 and *meso*inositol (II) (A., 1936, 1376) is not identical with the inosose (III) obtained by Kluyver *et al.* (A., 1940, III, 75) by the action of *Acetobacter suboxydans* on (II). (III), m.p. 200—202° (decomp.) when rapidly heated, is optically inactive and, like (I), very strongly reducing; the *phenylhydrazone* has m.p. 184° (decomp.) when rapidly heated. (III) is converted by Ac_2O in presence of H_2SO_4 or $ZnCl_2$ into a *penta-acetate*, which when cryst. from AcOH or Ac_2O containing the same catalysts has m.p. 211° (IV), but when cryst. from EtOH or from AcOH or Ac_2O in absence of catalysts has m.p. 147° (V); (V) yields (IV) when cryst. from Ac_2O or AcOH containing H_2SO_4. (IV) and (V) are probably not dimorphs. Similarly, (III) gives two *pentabenzoates*, m.p. 188° (VI) and 286° (VII). The acyl compounds show the reactions observed (*loc. cit.*) for the similar derivatives of (I). With Ac_2O in presence of basic catalysts (NaOAc, C_5H_5N) (IV) and (V) afford 1 : 2 : 3 : 5-$C_6H_2(OAc)_4$ and (VI) and (VII) give 1 : 2 : 3 : 5-$OH{\cdot}C_6H_2(OBz)_3$. (III) in aq. AcOH is readily reduced by Na–Hg to a mixture of about equal parts of (II) and (probably) scyllitol (VIII), m.p. 352° (corr.; block) [hexa-acetate, m.p. 298—299° (corr.; block)]. Catalytic hydrogenation (PtO_2) in neutral aq. solution converts (III) into (II) with a very small proportion of (VIII), whereas in dil. H_2SO_4 the product is *deoxyinositol* [*pentahydroxycyclohexane*], m.p. 233—235° after softening [*penta-acetate* (IX), m.p. 190°]. Catalytic hydrogenation of (IV) and (V) in AcOH–conc. H_2SO_4 gives essentially (IX); in AcOH alone the main product is an inositol penta-acetate, m.p. 161—162° (acetylated to *meso*inositol hexa-acetate), with possibly a small proportion of the penta-acetate of (VIII). H. W.

Cyclitols. VI. Configuration of *meso*inositol, scyllitol, and an inosose (scyllo-*meso*inosose) obtained biochemically. T. Posternak (*Helv. Chim. Acta*, 1942, **25**, 746—752; cf. A., 1942, II, 13).—The scyllitol obtained by reduction of the inosose (I) formed from *meso*inositol by *Acetobacter suboxydans* is identified by a mixed m.p. (I) is oxidised by $KMnO_4$–Na_2CO_3 to *dl*-idosaccharic acid [*K* and *Cu* ($+2H_2O$) salts; $(CHPh{:})_2$ derivative, m.p. ~245° (decomp.), and its Me_2 ester, m.p. 272°], obtained also from *d*- and *l*-xylose by addition of HCN, hydrolysis, oxidation, and combining the products. (I) is thus the $\frac{2:4:6}{3:5}$ compound, position of the numeral indicating the position of the OH on the C named relevant to the C_6-ring in the graphical formula. R. S. C.

Indones. XVII. Reactions of 3-phenyl-2-methylindone and 3-phenyl-2-ethylindone. R. de Fazi, F. Pirrone, and L. Rossetti Conti (*Gazzetta*, 1941, **71**, 153—163; cf. A., 1939, II, 377).—3-Phenyl-2-methylindone (I) is unchanged by HCl–Et_2O, which converts the oxime (II) of (I) into its *hydrochloride*, m.p. 198—199° (after changing colour from 80°). 2 : 3-Dichloro-3-phenyl-2-methylhydrindone, m.p. 92—93°, with HCl–Et_2O gives its isomeride, m.p. 111—113°. With Br–AcOH–Et_2O, (II) (which is unchanged by Cl_2–$CHCl_3$) gives a *product*, m.p. 128—135°, containing Br. KOH–EtOH and (I) give a *diphenyldimethyltruxone*, m.p. 242—244° (*oxime*, m.p. 239—240°). 3-Phenyl-2-ethylindone (III) is unchanged by HCl–Et_2O, as is the oxime of 2 : 3-dichloro-3-phenyl-2-ethylhydrindone (IV), m.p. 96°. With HCl–Et_2O, (IV) gives its isomeride, m.p. 115—116°. In addition to its oxime (V) of m.p. 186—187°, obtained in EtOH at the b.p., (III) forms at room temp. an isomeric *oxime* (VI), m.p. 175—176°. Both (V) and (VI) with boiling Ac_2O–AcCl form the same *Ac* derivative (VII), m.p. 147—148°. HCl–Et_2O converts (V) into its *hydrochloride* (VIII), decomp. from 70°, and (VII) into (VIII). With NH_3, (VII) gives (V). With Cl_2–CCl_4, (V) (which is unchanged by Br–AcOH) gives a Cl_2-derivative, m.p. 167—168° (decomp.). E. W. W.

Anils of cyclic diketones. P. Pfeiffer and T. Hesse (*J. pr. Chem.*, 1941, [ii], **158**, 315—320).—Indan-2-one (I) (prep. from indene by way of the bromohydrin modified) and PhNO with a little NaOEt in EtOH at 60—80° give 1 : 3-*dianiloindan*-2-*one*, m.p. 204°, green, and a red compound. However, *p*-$NO{\cdot}C_6H_4{\cdot}NMe_2$ (II), (I), and a little aq. NaOH in EtOH give the *compound*, *o*-$C_6H_4{<}\begin{matrix}C{:}[N(:O){\cdot}C_6H_4{\cdot}NMe_2]\\C{:}[N(:O){\cdot}C_6H_4{\cdot}NMe_2]\end{matrix}{>}CO$, m.p. 228° (decomp.) (cf. Ruhemann, *J.C.S.*, 1911, **99**, 797). *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$, (I), and NaOEt in EtOH give 1 : 3-*dianisylideneindan*-2-*one*, m.p. 165° (black *perchlorate*). Flavanone, (II), and a little aq. NaOH in EtOH give 3-p-*dimethylaminoanilo*flavanone, orange-red, m.p. 149°, and dark red, m.p. 153°, *forms*, stable in air. 1-Keto-1 : 2 : 3 : 4-tetrahydronaphthalene and (II) give similarly 1-*keto*-2 : 4-*di*-p-*dimethylaminoanilo*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, violet, m.p. 217°, converted by boiling dil. H_2SO_4 into 2-hydroxy-1 : 4-naphthaquinone. R. S. C.

Action of *coli* bacteria on dehydronorcholene. A. Butenandt and H. Dannenberg (*Naturwiss.*, 1942, **30**, 52).—All types of *coli*, whether or not derived from cancerous sources, degrade dehydronorcholene (I) oxidatively in presence of air at 37° provided that the nutrient contains little or no peptone. One product is 22-*ketodehydronorcholene* (II), m.p. 157°, $[\alpha]_D$ +81·5° in EtOH (*oxime*, m.p. 175—176°), also obtained from (I) and CrO_3 at 55°. (II) is (absorption spectrum) an αβ-unsaturated ketone. (I) is gradually degraded completely by *B. coli* but a cryst. product other than (II) has not been isolated. (II) is only an intermediate but the production of methylcholanthrene or a related aromatic compound has not been detected. H. W.

New *iso*naphthazarin synthesis. F. Weygand (*Ber.*, 1942, **75**, [*B*], 625—626).—The action of air on a solution of *o*-$C_6H_4(CHO)_2$, $[CH(OH){\cdot}SO_3Na]_2$, and KCN in dioxan–2N-Na_2CO_3 leads to *iso*-

naphthazarin, m.p. 287°. Condensation succeeds in the region p_H 8—12 and requires the presence of CN′. Methyl- and phenylglyoxal do not condense similarly. H. W.

Sulphur derivatives of 3-amino-1 : 2-benzanthraquinone.—See B., 1942, II, 362.

IV.—STEROLS AND STEROID SAPOGENINS.

Glucoside formation from epimeric alcohols.—See A., 1942, II, 351.

Unsaponifiable matter of human serum.—See A., 1942, III, 799.

Directions of the development of the synthetic preparation of natural steroid hormones. A. Butenandt (*Naturwiss.*, 1942, **30**, 4—17).

Transformation of steroid hormones into the methyl homologues of *cyclo*pentenophenanthrene. A. Butenandt and L. A. Surányi (*Ber.*, 1942, **75**, [*B*], 597—606).—Δ^5-Androstenediol is converted by Se at 310—320° into 3′-methyl*cyclo*pentenophenanthrene (**I**), m.p. 125—126° [*picrate*, m.p. 115—116°; compounds, m.p. 150—151° and 92°, with 1 : 3 : 5-$C_6H_3(NO_2)_3$ and 1 : 2 : 4 : 6-$C_6H_2Me(NO_2)_3$ respectively]. Δ^5-Androsten-3-ol is converted by BzO_2H in $CHCl_3$ into its 5 : 6-*oxide*, m.p. 151—152°, which with MgMeI followed by Ac_2O yields 6-*methylandrostane*-3 : 5-*diol* 3-*acetate*, m.p. 137—138°, dehydrogenated by Se at 320—330° to 9-methyl*cyclo*pentenophenanthrene (**II**), m.p. 109—110°, softens at 106°. Similarly, Δ^5-androstene-3 : 17-diol diacetate is transformed into 9 : 3′-dimethyl*cyclo*pentenophenanthrene (**III**), m.p. 78—78·5°. Δ^2(?)-Androstene-6 : 17-dione and MgMeI afford Δ^2(?)-6 : 17-*dimethylandrostene*-6 : 17-*diol* (+H_2O), m.p. 80—85°, dehydrogenated by Se at 310—330° to 9 : 3′ : 3′-*trimethyl*cyclo*pentenophenanthrene* (**IV**), m.p. 96—97° [*picrate*, m.p. 154—155°; styphnate, m.p. 159—160°; compound, m.p. 160—161°, with 1 : 3 : 5-$C_6H_3(NO_2)_3$], also obtained from dehydroandrosterone by successive treatments with BzO_2H, MgMeBr, and Se. Et 2-methyl*cyclo*pentanone-2-carboxylate, $NaNH_2$, and MeBr in Et_2O yield Et 2 : 5-dimethyl*cyclo*pentanone-2-carboxylate, b.p. 110—125°/12 mm., hydrolysed and decarboxylated by boiling conc. HCl to 2 : 5-dimethyl*cyclo*pentanone, b.p. 146—147°/766 mm. (*semicarbazone*, m.p. 196—197°). It is very unlikely that (**I**), (**II**), (**III**), or (**IV**) has carcinogenic activity. H. W.

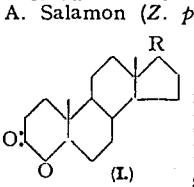
Steroids. XXX. Ability of epimeric steroid alcohols to add acid. K. Miescher and H. Kägi (*Helv. Chim. Acta*, 1941, **24**, 986—988).—In boiling EtOAc the following give additive *compounds* (2 : 1) with $H_2C_2O_4$: 3*t*-cholesterol, m.p. ~160° (decomp.), re-solidifies with m.p. 195°; 3*t*-cholestanol, m.p. ~170° (decomp.); 3*t*-dehydroandrosterone, m.p. 144—145·5° (decomp.), partly re-solidifying with m.p. ~200°; 3*t*-androsterone, m.p. 139—140° (decomp.), re-solidifies with m.p. 200°. Compounds were not obtained with any *epi*-steroid or with 3*t*-ergosterol, Δ^5-androstene-3*t* : 17*t*-diol, Δ^5-pregnenolone, Δ^5-norcholesten-3*t*-ol-25-one, the two coprosterols, and 3*t*-cholesteryl acetate. The ability to form these additive compounds may be connected with the presence of a free *t* (=transoid)-OH. H. W.

Configurative connexion of 17(α)-hydroxypregnane derivatives with glycerol side-chain which are epimeric with regard to position 20. H. Reich, C. Montigel, and T. Reichstein (*Helv. Chim. Acta*, 1941, **24**, 977—985).—17-Vinyl-Δ^5-androstene-3(β) : 17(α)-diol 3-monoacetate with OsO_4 in abs. Et_2O at room temp. followed by aq. Na_2SO_3 and acetylation gives Δ^5-pregnene-3(β) : 17(α) : 20(α) : 21-tetrol 3 : 20 : 21-triacetate (**I**), m.p. 166—168°, $[\alpha]_D^{19}$ −90·8°±4° in $COMe_2$, identical with the product of Serini *et al.* (A., 1938, II, 322), and the corresponding 20(β)-*isomeride* (**II**), m.p. 123—125°, $[\alpha]_D^{19}$ −44·2°±3° in $COMe_2$. The assignation of formulæ depends on hydrogenation which leads to known triacetates. (**I**) is hydrolysed to the tetraol, which with $COMe_2$ and anhyd. $CuSO_4$ affords Δ^5-*pregnene*-3(β) : 17(α) : 20(α) : 21-*tetraol* 20 : 21-*CMe*$_2$: *ether* (**III**), granules or coarse prisms, m.p. (mainly) 124—130°, softens at 120°, partly re-solidifies and melts at 156—158°, $[\alpha]_D^{13\cdot5}$ −62·7°±2° in $COMe_2$; the 20(β)-*isomeride* (**IV**), m.p. (mainly) ~100° and 148—161° after partial re-solidification, $[\alpha]_D^{15}$ −59·0°±2° in $COMe_2$, does not appreciably depress the m.p. of (**III**). $Al(OBu^{\gamma})_3$ converts (**III**) in boiling C_6H_6–$COMe_2$ into Δ^4-*pregnene*-17(α) : 20(α) : 21-*triol*-3-*one* 20 : 21-*CMe*$_2$: *ether* (**V**), m.p. 220—221·5° $[\alpha]_D^{15}$ +66·7°±2° in $COMe_2$, and (**IV**) into the 20(β)-*derivative* (**VI**), m.p. 173—175°, $[\alpha]_D^{17}$ +39·3°±2° in $COMe_2$. Hydrolysis followed by acetylation converts (**V**) into Δ^4-*pregnene*-17(α) : 20(α) : 21-*triol*-3-*one* 20 : 21-*diacetate*, m.p. 165—166°, $[\alpha]_D^{15}$ +21·6°±3° in $COMe_2$, and (**VI**) into the 20(β)-isomeride, m.p. 180—181°, $[\alpha]_D^{15}$ +50·2°±2° in $COMe_2$, identical with the compound of Serini (*loc. cit.*). Acetates of the β-series have invariably a higher +-rotation than those of the α-series. With CMe_2: compounds the opposite is frequently true but there is no general rule. M.p. are corr. H. W.

Preparation of deoxycholic acid. G. A. D. Haslewood (*Nature*, 1941, **150**, 211).—Cholic acid from bile is oxidised with CrO_3 to a mixture containing ~45% of 3 : 12-dihydroxy-7-ketocholanic acid which is reduced to deoxycholic acid. A. A. E.

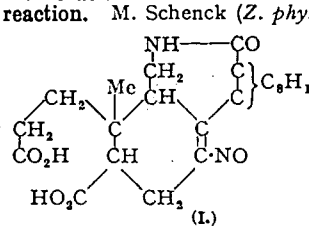
Δ^5-Pregnene-3(β) : 17(α)-diol-20-carboxylic acid and its transformation products. A. Lardon and T. Reichstein (*Helv. Chim. Acta*, 1941, **24**, 1127—1140; cf. A., 1939, II, 318).—CHMeBr·CO_2Et, Zn, and Δ^5-androsten-3(β)-ol-20-one acetate give a small amount of acidic products from which (?) $\Delta^{5:17}$-*pregnadien*-3(β)-*ol*-20-*carboxylic acid*, m.p. 124—126°, $[\alpha]_D^{21}$ −176·5° in $COMe_2$ (non-cryst. acetate), is readily isolated and mainly neutral compounds which after hydrolysis yield Δ^5-*pregnene*-3(β) : 17(α)-*diol*-20-*carboxylic acid*, m.p. 230—234° [*Me* ester (**I**), m.p. 182—183°, $[\alpha]_D^{21}$ −61·1°±2° in $COMe_2$, and its 3-*monoacetate*, m.p. 201—204°, $[\alpha]_D^{21}$ −67·0°±2° in $COMe_2$, which is not further acetylated by Ac_2O and C_5H_5N at 100°], and an isomeric acid isolated as the *Me* ester *acetate*, m.p. 164—166°, $[\alpha]_D^{21}$ −71·1°±2° in $COMe_2$. (**I**) is reduced by Na and EtOH and then acetylated (Ac_2O–C_5H_5N at room temp.) to 20-*methyl*-Δ^5-*pregnene*-3(β) : 17(α) : 21-*triol* 3 : 21-*diacetate* (**II**), m.p. 162—163°, hydrolysed (KOH–aq. MeOH) to the *triol*, m.p. 206—209°. $POCl_3$ in boiling abs. C_5H_5N transforms (**II**) into (?) 20-*methyl*-$\Delta^{5:16}$-*pregnadiene*-3(β) : 21-*diol diacetate* (**III**), m.p. 114—116°, $[\alpha]_D^{21}$ −40·5°±2° in $COMe_2$, with smaller proportions of an *isomeride*, m.p. 99—102°, and a *compound* (? mixture), $C_{26}H_{40}O_5$, m.p. 156—160°. (**II**) is hydrogenated (PtO_2 in AcOH) to 20-methyl*allo*pregnane-3(β) : 17(α) : 21-triol 3 : 21-diacetate, m.p. 184—186°, which does not yield homogeneous crystals when dehydrated by $POCl_3$ and C_5H_5N; the main product is probably 20-methyl-Δ^{16}-*allo*pregnene-3(β) : 21-diol diacetate since it does not afford androstan-3(β)-ol-17-one acetate when ozonised. (**III**) is converted by successive treatments with OsO_4 in Et_2O, Na_2SO_3, and Ac_2O–C_5H_5N into (?) 20-*methyl*-Δ^5-*pregnene*-3(β) : 16 : 17 : 21-*tetraol* 3 : 16 : 21-*triacetate*, m.p. 167—168°, $[\alpha]_D^{17}$ −119·6°±3° in $COMe_2$, hydrogenated (PtO_2 in AcOH) to the saturated *triacetate*, m.p. 135—137°, $[\alpha]_D^{19}$ −64·4°±3° in $COMe_2$, which is hydrolysed to (?) 20-*methyl*allo*pregnane*-3(β) : 16 : 17 : 21-*tetraol*, m.p. 232—237°. This does not give cryst. products when oxidised with HIO_4 or CrO_3–AcOH and therefore cannot be 20-methyl*allo*pregnane-3(β) : 17(β) : 20 : 21-tetraol. M.p. are corr. H. W.

Oxidation of cholestenone and progesterone by persulphuric acid. A. Salamon (*Z. physiol. Chem.*, 1941, **272**, 61—64).—Cholestone in AcOH is slowly oxidised by $K_2S_2O_8$–H_2SO_4 at room temp. to 5-*hydroxynor*-(4)-4‖5-*coprostano*-3-*lactone* [(**I**); R = C_8H_{17}], m.p. 111°, $[\alpha]_D^{22}$ +90° in 96% EtOH, which does not absorb H_2 in presence of Pd–C, does not react with NH_2·CO·NH·NH_2, is insol. in Na_2CO_3 but sol. in warm aq. KOH and pptd. unchanged when the solution is acidified. Similarly progesterone affords 5-*hydroxynor*-(4)-4‖5-*pregnan*-20-*one*-3-*carboxylolactone* [(**I**); R = COMe], m.p. 154° (*semicarbazone*, decomp. 260—264°).


(I.)

H. W.

Bile acids. LXVII. Oxido-reduction of the type of Cannizzaro reaction. M. Schenck (*Z. physiol. Chem.*, 1941, **272**, 52—60).—The prep. of the corresponding NO_2-acids from the acids (**I**), (**II**), and (**III**) is described. Evidence is adduced in favour of the view that the reaction of (**I**), (**II**), and (**III**) with H_2SO_4 is an oxido-reduction change whereby part of the acid is converted into the ketoxime acid which is stable in solution and the other part is oxidised to the NO_2-acid which immediately or speedily is changed in an unelucidated manner.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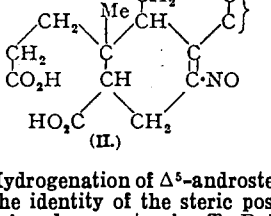
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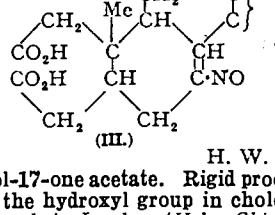

(III.)

H. W.

Hydrogenation of Δ^5-androsten-3(β)-ol-17-one acetate. Rigid proof of the identity of the steric position of the hydroxyl group in cholesterol and corposterol. T. Reichstein and A. Lardon (*Helv. Chim. Acta*, 1941, **24**, 955—961).—Δ^5-Androsten-3(β)-ol-17-one acetate (*t*-dehydroandrosterone acetate) is hydrogenated (PtO_2 in AcOH) to a mixture of androstan-3(β)-ol-17-one acetate and ætiocholan-3(β)-ol-17-one acetate (**I**), m.p. 157—159°, $[\alpha]_D^{17}$ +81·9°±2° in $COMe_2$ (semicarbazone, m.p. 248—250°), which is hydrolysed to ætiocholan-3(β)-ol-17-one, m.p. 152—154°, $[\alpha]_D^{20}$ +88·8°±2° in EtOH, oxidised to ætiocholane-3 : 17-dione, m.p. 132—134°, $[\alpha]_D^{17}$ +110·5°±3° in abs. EtOH. The prep. of (**I**) from coprosterol is described. This is the first instance of the formation of coprostane derivatives by the hydrogenation of steroids with double linking at $C_{(5)}$ and the course of the reaction is a rigid proof that OH of cholesterol and coprosterol has the same steric position. H. W.

Steroids and sex hormones. LXX. Dihydrotestosterone H succinate. L. Ruzicka, M. W. Goldberg, and C. Grob (*Helv. Chim. Acta*, 1941, **24**, 1151—1154).—Δ^5-3-Acetoxyandrosten-17-ol and $(CH_2{\cdot}CO)_2O$ in abs. C_5H_5N at 85° give Δ^5-*androstene*-3 : 17-*diol* 3-*acetate* 17-*H succinate*, m.p. 160·5—161·5°, hydrolysed by $KHCO_3$ in boiling aq. MeOH to Δ^5-*androstene*-3 : 17-*diol* 17-*H succinate*, m.p. 205—206° (*Me* ester, m.p. 106°). This is hydrogenated (PtO_2 in AcOH at room temp.) to *androstane*-3 : 17-*diol* 17-*H succinate*, m.p. 225·5—226·5°, oxidised by CrO_3 to *androstan*-17-*ol*-3-*one* 17-*H succinate*, m.p. 135·5° (opaque) and 168·5° after re-solidification when rapidly heated, which is hydrolysed to androstan-17-ol-3-one. M.p. are corr. H. W.

Derivatives of *i*-androstane. A. Butenandt and L. A. Surányi (*Ber.*, 1942, **75**, [*B*], 591—597).—Dehydroandrosterone is converted by *p*-$C_6H_4Me{\cdot}SO_2Cl$ and C_5H_5N into the 3-*p*-toluenesulphonate, m.p. 153—154°, converted by KOAc and boiling 50% $COMe_2$ followed by Ac_2O into the *acetate* (**I**), m.p. 113—114°, $[\alpha]_D^{20}$ +117·5° in EtOH, of i-*androstan*-6-*ol*-17-*one* (**II**), m.p. 136—138°, $[\alpha]_D^{20}$ +122° in EtOH (semicarbazone, m.p. 237—240°), which is stable towards BzO_2H and hydrogenation (PtO_2 in EtOH). AcOH and 48% HBr convert (**I**) into 3-*bromo*-Δ^5-*androsten*-17-*one*, m.p. 174°, transformed by AgOAc in boiling AcOH into dehydroandrosterone acetate. Hydrogenation (PtO_2 in AcOH) of (**I**) gives presumably androstan-17-ol, m.p. 158—159° (acetate, m.p. 75—76°). (**II**) is oxidised (CrO_3 in AcOH at 10°) to i-*androstane*-6 : 17-*dione* (**III**), m.p. 182—183°, $[\alpha]_D^{20}$ +113° in $CHCl_3$ (*dioxime*, m.p. 269—271°), which does not show the absorption characteristic of $\alpha\beta$-unsaturated ketones, is stable towards hydrogenation (Pd–$CaCO_3$ in EtOH) and physiologically inactive. (**III**) and 5N-H_2SO_4 in boiling AcOH yield *androstan*-3-*ol*-6 : 17-*dione acetate*, m.p. 197—198°. Reduction of (**III**) by fermenting yeast and acetylation of the product leads to i-*androstan*-17-*ol*-6-*one acetate*, m.p. 109—110°. HBr (48%) in boiling AcOH transforms (**III**) into 3-*bromoandrostane*-6 : 17-*dione* (**IV**), m.p. 184°, reconverted into (**III**) by boiling collidine or KOAc–AcOH. Boiling quinoline (N_2) transforms (**IV**) into (?) Δ^2-*androstene*-6 : 17-*dione* (**V**), m.p. 191—191·5°, $[\alpha]_D^{20}$ +126° in EtOH, which is stable towards HBr–AcOH, it is also obtained similarly from (**III**) and is converted by BzO_2H into an *oxide*, m.p. 174—176°. (**V**) is hydrogenated (Pd–$CaCO_3$ in EtOH) to *androstane*-6 : 17-*dione*, m.p. 134—135° (*dioxime*, m.p. 288—290°). Dehydroandrosterone-semicarbazone and NaOEt in EtOH at 145° afford Δ^5-*androsten*-3-*ol*, m.p. 131°, $[\alpha]_D^{20}$ −48° in EtOH (*acetate*, m.p. 91—93°); the 3-*p*-*toluenesulphonate*, m.p. 136°, is isomerised and then oxidised to i-*androstan*-6-*one*, m.p. 122—122·5°, $[\alpha]_D^{20}$ +34·5° in EtOH. H. W.

Constituents of the adrenal gland and related substances. XLIX. Partial synthesis of Δ^5-pregnene-3(β) : 17(β) : 21-triol-20-one and Δ^5-pregnene-3(β) : 17(β)-diol-20-one. H. G. Fuchs and T. Reichstein (*Helv. Chim. Acta*, 1941, **24**, 804—828).—Δ^5-Allylandrostene-3(β) : 17(α)-diol 3-acetate is dehydrated by $POCl_3$ in boiling C_5H_5N to $\Delta^{5:17:21}$-ω-*homopregnatrien*-3(β)-*ol acetate*, m.p. (indef.) 201—210°, which is converted (OsO_4 in Et_2O, than aq. EtOH–Na_2SO_3) into Δ^5-ω-*homopregnene*-3(β) : 17(β) : 20(β) : 21(β) : 22-*pentaol* (**I**) (+1·5H_2O), m.p. 246—257° (slight decomp.), $[\alpha]_D^{15}$ −61·0°±2·5° in EtOH, $\Delta^{5:17}$-ω-*homopregnadiene*-3(β) : 21(α) : 22-*triol* (**II**), m.p. 162—164°, $[\alpha]_D^{14}$ −76·1°±3° in dioxan, and $\Delta^{5:17}$-ω-*homopregnadiene*-3(β) : 21(β) : 22-*triol* (**III**), m.p. 194·5—196°, $[\alpha]_D^{14}$ −48·2°±3° in dioxan. (**I**) is hydrogenated (PtO_2 in AcOH–EtOH) and then oxidised (CrO_3 in AcOH) to androstane-3 : 17-dione. (**II**) is transformed by HIO_4 followed by Ac_2O–C_5H_5N into $\Delta^{5:17}$-pregnadien-3(β)-ol-21-al acetate (**IV**), m.p. 180—187°, and by hydrogenation followed by oxidation and methylation into *Me* 3-*ketoandrostanyl*-17-*acetate*, m.p. 138·5—140°, also obtained by hydrolysis, methylation, and oxidation of Me 3(β)-acetoxyandrostanyl-17-acetate. (**III**) is oxidised (HIO_4) and then acetylated to (**IV**). Further by-products of (**I**) are described. (**I**) and $COMe_2$ containing $CuSO_4$ at room temp. afford the 21 : 22-*CMe*$_2$: *ether* (**V**), m.p. 180·5—182° and, after re-solidification, m.p. 191—192°, $[\alpha]_D^{11}$ −37·6°±1·5° in $COMe_2$, the 3 : 20-*diacetate* (**VI**), m.p. 215—219°, $[\alpha]_D^{16}$ −12·0°±3° in $COMe_2$, of which is hydrogenated (PtO_2 in EtOH–EtOAc) to *allo*-ω-homopregnane-3(β) : 17(β) : 20(β) : 21(β) : 22-pentaol 21 : 22-CMe_2 : ether 3 : 20-diacetate, m.p. 213°, $[\alpha]_D^{16}$ +33·0°±2° in $COMe_2$, hydrolysed (MeOH–KOH) to the pentaol 21 : 22-CMe_2 : ether, m.p. 205—207°. (**VI**) is hydrolysed (aq. AcOH) to an amorphous product which is degraded by HIO_4 to Δ^5-*pregnene*-3(β) : 17(β) : 20(β)-*triol*-21-*al* 3 : 20-*diacetate* (**VII**), m.p. 164—165° (slight decomp.), $[\alpha]_D^{15}$ −24·4°±3° in dioxan; this is hydrolysed ($KHCO_3$ in MeOH) to the aldehyde, which is transformed by successive treatments with abs. C_5H_5N and Ac_2O into Δ^5-*pregnene*-3(β) : 17(β) : 21-*triol*-20-*one* 3 : 21-*diacetate*, m.p. 198—200° after becoming altered at ~178°, $[\alpha]_D^{16}$ −15·3°±3° in $CHCl_3$. This is converted by MgMeBr in Et_2O–PhMe into a mixture which is resolved by HIO_4 into Δ^5-pregnene-3(β) : 17(β)-diol-20-one, m.p. 286° after sometimes melting at ~270°, $[\alpha]_D^{16}$ −34·9°±4° in EtOH–dioxan (2 : 1), and Me Δ^5-3(β) : 17(β)-dihydroxyætiocholenate, m.p. 231—238°. (**VII**) is hydrogenated (PtO_2 in AcOH) and then acetylated to *allo*pregnene-3(β) : 17(β) : 20(β) : 21-tetraol 3 : 20 : 21-triacetate, m.p. 172—174°, $[\alpha]_D^{14}$ +53·7°±3° in $COMe_2$, identical with *K* triacetate. (**II**) is converted by $COMe_2$–$CuSO_4$ followed by acetylation into $\Delta^{5:17}$-ω-*homopregnadiene*-3(β) : 21(α) : 22-*triol* 21 : 22-*CMe*$_2$: *ether* 3-*acetate*, m.p. 167—168°, $[\alpha]_D^{14}$ −56·1°±2° in $COMe_2$, which is transformed by successive treatments with OsO_4 in Et_2O etc. and Ac_2O–C_5H_5N into Δ^5-ω-*homopregnene*-3(β) : 17(β) : 20(β) : 21(α) : 22-*pentaol* 21 : 22-*CMe*$_2$: *ether* 3 : 20-*diacetate*, m.p. 210—220°, $[\alpha]_D^{16}$ −36·8°±4° in $COMe_2$; this is converted into the pentaol diacetate, which is degraded (HIO_4) to (**VII**). (**III**) is converted by $COMe_2$–$CuSO_4$ followed by Ac_2O–C_5H_5N into $\Delta^{5:17}$-ω-*homopregnadiene*-3(β) : 21(β) : 22-*triol* 21 : 22-*CMe*$_2$: *ether* 3-*acetate*, m.p. 169—171°, $[\alpha]_D^{13}$ −33·5°±3° in $COMe_2$, converted by the successive actions of OsO_4 in Et_2O at room temp. and Ac_2O into (**V**). M.p. are corr. H. W.

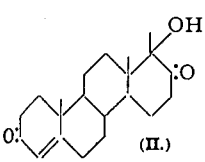
Constituents of the adrenal gland and related substances. L. Simplified partial synthesis of substance *L* and Δ^5-pregnene-3(β) : 17(β)-diol-20-one. P. Hegner and T. Reichstein (*Helv. Chim. Acta*, 1941, **24**, 828—844).—Δ^5-Pregnene-3(β) : 21-diol-20-one 21-acetate is converted by successive treatments with MgMeBr and Ac_2O–C_5H_5N at room temp. into the diacetate and a mixture of the *diacetate* (**I**), m.p. 170—172°, $[\alpha]_D^{17}$ −46·6°±2° in $COMe_2$, of Δ^5-20-methylpregnene-3(β) : 20(α) : 21-triol (**II**), m.p. 235—237°, and the *diacetate* (**III**), m.p. 194—196°, $[\alpha]_D^{13}$ −57·9°±1·5° in $CHCl_3$, of Δ^5-20-methylpregnene-3(β) : 20(β) : 21-triol (**IV**), m.p. 246—255°. (**II**) and (**IV**) are converted by HIO_4 into pregnenolone. (**I**) and (**III**) are reduced (H_2, PtO_2, AcOH) to 20-*methyl*allo*pregnane*-3(β) : 20(α) : 21-*triol* 3 : 21-*diacetate* (**V**), m.p. 189—190°, and the 3(β) : 20(β) : 21-triol 3 : 21-diacetate, m.p. 221—223°, respectively. (**V**) is converted by $POCl_3$ in boiling C_5H_5N into a mixture which is directly hydroxylated (OsO_4) and then oxidised by HIO_4 to 3-hydroxyætio*allo*cholanic acid and substance *L* isolated as the acetate, m.p. 234—235°, $[\alpha]_D^{15}$ −40·9°±1° in dioxan. (**I**) is similarly converted by successive treatments with $POCl_3$, OsO_4, and HIO_4 into Δ^5-3-hydroxyætiocholenic acid and Δ^5-pregnene-3(β) : 17(β)-diol-20-one 3-acetate, m.p. 234—235°, $[\alpha]_D^{15}$ −40·9°±1° in dioxan, hydrolysed to the (OH)$_2$-ketone (**VI**), m.p. ~287° after partial or complete melting at 271—273°, $[\alpha]_D^{15}$ −37·2°±3° in dioxan. Similar treatment of (**III**) gives Δ^5-pregnene-3(β) : 17(β)-diol-20-one 3-acetate, m.p. 234—235°, $[\alpha]_D^{15}$ −41·8°±2·5° in dioxan. This could not be hydrogenated in presence of Pd–$CaCO_3$ but with PtO_2–AcOH and subsequent acetylation gives *J* and *O* diacetates. Oxidation of (**VI**) by $Al(OBu^{\gamma})_3$ gives 17(α)-methyl-Δ^4-D-homoandrosten-17(α)-ol-3 : 17-dione, m.p. 288—289°, $[\alpha]_D^{13}$ +60°±16° in dioxan; CrO_3 affords apparently 17(β)-hydroxyprogesterone. M.p. are corr. H. W.

Constituents of the adrenal cortex and related compounds. LIII. Simplified method of preparing 17(β)-hydroxypregnane derivatives with dihydroxy-aldehyde- and -acetone-groups in the side chain. J. von Euw and T. Reichstein (*Helv. Chim. Acta*, 1941, **24**, 1140—1142; cf. A., 1941, II, 46).—ω-Homo-Δ^4-pregnene-17(β) : 20(β) : 21(β) : 22-tetraol-3-one, m.p. 238—245°, is oxidised by HIO_4 in dioxan and the product is treated with C_5H_5N at 111° and acetylated; substance *S*-acetate, m.p. 235—237° (yield ~30%), and Δ^4-androstene-3 : 17-dione are obtained. M.p. are corr. H. W.

Constituents of the adrenal gland and related substances. LII. Partial syntheses of 17(β)-hydroxyprogesterone and substance *L*. D. A. Prins and T. Reichstein (*Helv. Chim. Acta*, 1941, **24**, 945—955).—*allo*Pregnane-3(β) : 17(β) : 20(β) : 21-tetraol is converted by HIO_4 in dioxan into 17-*formylandrostane*-3(β) : 17(β)-*diol*, m.p. 187—190°, which rapidly reduces warm Ag_2O–NH_3 and gives a pronounced red colour with 1 : 4-$C_{10}H_6(OH)_2$. It is transformed by CH_2N_2 followed by Ac_2O in C_5H_5N into the acetate of substance *L*, m.p. 187—189°, $[\alpha]_D^{16}$ +15·9°±4° in $COMe_2$. Similarly, Δ^4-pregnene-17(β) : 20(β) : 21-triol-3-one gives Δ^4-17-formylandrosten-17(β)-ol-3-one, m.p. 162—164°, $[\alpha]_D^{13}$ +47·7°±2° in $COMe_2$, transformed by HIO_4 in aq. dioxan at room temp. into Δ^4-androstene-3 : 17-dione (**I**), m.p. 172—174°, and by CH_2N_2 in dioxan into 17(β)-hydroxyprogesterone, m.p. 218—220° when slowly heated, $[\alpha]_D^{17}$ +98·8°±5° in $COMe_2$, which is oxidised by CrO_3 in AcOH to (**I**). Δ^4-Pregnene-17(α) : 20(β) : 21-triol-3-one and HIO_4 in aq. dioxan afford Δ^4-17-*formylandrosten*-17(α)-*ol*-3-*one*, m.p. 133—135°, $[\alpha]_D^{13}$ +80·8°±2° in $COMe_2$, which yields a *compound*, m.p. 200—202°, $[\alpha]_D^{13}$ +64·9°±2° in $COMe_2$, when sublimed at 130—150°/0·01 mm., and is oxidised by HIO_4 to (**I**). It is slowly transformed by CH_2N_2 at room temp. into 20 : 21-*oxido*-Δ^4-*pregnen*-17(α)-*ol*-3-*one* (**II**), m.p. 202—204°, $[\alpha]_D^{13}$ +73·0°±2° in $COMe_2$, and a compound, m.p. 172—174°, which do not react with 1 : 4-$C_{10}H_6(OH)_2$ or Ag_2O–NH_3 and are relatively stable to CrO_3, and a *compound*, $C_{21}H_{30}O_3$, m.p. 200—201°, $[\alpha]_D^{13}$ +32·8°±3° in $COMe_2$, which rapidly reduces CrO_3 in AcOH. Isolation of (**II**) is easier if the crude product is treated with HIO_4 to remove unchanged aldehyde. (**II**) is also obtained by oxidising vinyltestosterone with BzO_2H in $CHCl_3$. M.p. are corr. H. W.

Constituents of the adrenal gland and related substances. LI. 17(β)-Hydroxyprogesterone. J. von Euw and T. Reichstein (*Helv. Chim. Acta*, 1941, **24**, 879—889).—The "A-residue A II" and "A-residue A III" (A., 1936, 1382) are treated with $KHCO_3$ in aq. MeOH at room temp. and then either acetylated and subjected directly to chromatography or purified by $(CH_2{\cdot}CO)_2O$ with which

only ketols with the side group $CO{\cdot}CH_2{\cdot}OH$ react completely. Direct crystallisation of the product gives 17(β)-hydroxyprogesterone



(I), m.p. 222—223° when not too slowly heated, $[\alpha]_D^{17}$ +105·6°±5° in $CHCl_3$. *allo*-Pregnan-3(β)-ol-20-one, progesterone, Δ^4-androstenedione, androstane-3(β) : 11-diol-17-one, and adrenosterone are obtained as by-products. When heated above its m.p. (I) is partly transformed into the chrysene derivative (II), m.p. 288—291°, and a *substance*, m.p. 162—164°, which appears isomeric with (I) and (II). Similar isomerisation is caused by $Al(OBu^v)_3$. Protracted heating of (I) with sufficiently conc. KOH–MeOH causes extensive transformation into (II) and an isomeric *compound*, m.p. 187°. M.p. are corr. H. W.

Saponins and sterols. X. Δ^1-Dehydro-Δ^4-androstene-3 : 17-dione. K. Fujii and T. Matsukawa (*J. Pharm. Soc. Japan*, 1930, **56**, 543—546).—5-Chloro-*trans*-androsterone (prep. from *trans*-dehydroandrosterone and HCl–$CHCl_3$) is oxidised (CrO_3) to *5-chloroandrostanedione*, m.p. 179° (decomp.), brominated to *5-chloro-2-bromoandrostanedione*, m.p. 156° (decomp.), which is dehalogenated (KOAc in AcOH) to *Δ^1-dehydro-Δ^4-androstenedione*, m.p. 168° (gives a positive Allen–Doisy test). M.p. are corr. CH. ABS. (*c*)

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Magnesium pinene chloride and the camphanecarboxylic acids. G. Vavon and C. Rivière (*Compt. rend.*, 1941, **213**, 1016—1018).—Mg pinene chloride (I) and CO_2 (excess) yield the two camphanecarboxylic acids in equal amounts. With less CO_2 or when heated in PhMe at 110° for 2—3 hr. and then treated with CO_2 (I) yields an *acid* (two forms), $[\alpha]_{5780}$ +11·9° in PhMe, m.p. 81·5—82·5° and 74·5—76°. Selective interaction of (I) with $CH_2{:}CH{\cdot}CH_2Br$ and treatment of the residue with CO_2 yields an *acid*, m.p. 76·5—77°, $[\alpha]_{5780}$ +45·1° in PhMe. It is concluded that (I) contains two simple isomerides (35% of each) and a double compound (30%). A. LI.

Optical activity of terpenes. II. Influence of the solvent on the rotation of bornyl and *iso*bornyl methyl ether. W. Hückel and H. Kaluba (*Annalen*, 1942, **550**, 269—287).—The influence of solvents on $[\alpha]$ (3 λ) of bornyl (20 solvents) and *iso*bornyl Me ether (13 solvents) is similar to but, as anticipated, < for borneol (6 additional solvents) and *iso*borneol (9 additional solvents). *Bornyl oxalate*, m.p. 108°, $[\alpha]_D$ −45·2° in C_6H_6, *p-nitrobenzoate*, m.p. 136°, $[\alpha]_D$ −33·1° in C_6H_6, *H succinate*, m.p. 60°, $[\alpha]_D$ −35·20° in EtOH, and *formate*, b.p. 215°, $[\alpha]_D$ −47·24° (homogeneous), are described. Other optical and physical data are recorded. R. S. C.

***cyclo*Hexanone series. Homonorcamphoric and norborneolcarboxylic acids.** H. Gault and K. W. Hiong (*Compt. rend.*, 1941, **213**, 353—354).—Et *cyclo*hexanone-2-carboxylate (I) with 35% CH_2O gives Et 2-hydroxymethyl*cyclo*hexanone-2-carboxylate (II) (90% yield), purified from (I) with NaOH. The *acetate*, b.p. 153—154°/1·5 mm., of (II) with KOH (cf. A., 1940, II, 130) yields *homonorcamphoric acid*, m.p. 85° (III) (by ring fission and recyclisation at $C_{(3)}$–$C_{(7)}$). (III) is isomeric with the acid of Hintikka and Komppa (A., 1918, i, 543) and is not a hexahydro*iso*phthalic acid. (III) affords an Et_2 ester, b.p. 146—147°/14 mm., which with Na gives *Et norcamphorcarboxylate* (IV), b.p. 126—127°/20 mm. (*hydrazone*, m.p. 182—183°). Hydrolysis of (IV) does not give a free acid or norcamphor. (IV) is reduced to the *Et* ester, b.p. 120—122°/18 mm. (*4c* derivative, b.p. 138—139°/20 mm.), of *norborneolcarboxylic acid*, m.p. 62—63°, which is not decarboxylated to norborneol. C. S.

Catalytic reduction of camphorquinone. H. Rupe and F. Müller (*Helv. Chim. Acta*, 1941, **24**, 1093).—Catalytic reduction in presence of Ni rapidly converts camphorquinone into a lævorotatory 2 : 3-*dihydroxycamphane*, m.p. 248—250°, probably a stereoisomeride of the compound of Manasse (A., 1903, i, 45). H. W.

Volatile vegetable compounds. XIV. Structure of caryophyllene. Y. R. Naves and E. Perrottet (*Helv. Chim. Acta*, 1941, **24**, 789—804).—Caryophyllene (I), obtained by distillation of the non-phenolic fraction of the hydrolysed oil of cloves, is a chemical individual. Its hydrogenation in presence of Pd gives a single dihydrocaryophyllene (II). Two non-conjugated ethylenic linkings are present in (I), one being contained in the CMe_2 group whereas the other is cyclic and based on the methylated *tert.* C. The Raman spectrum appears irreconcilable with the presence of a 7-C ring and no proof of the existence of such a ring has been adduced. (I), b.p. 103—103·5°/4 mm., α_D −8·16°, is reduced to (II), b.p. 119°/10 mm., α_D −25·68°, and (PtO_2) to tetrahydrocaryophyllene (III), b.p. 99·5—100°/3·5 mm., α_D −5·46°, which does not give a colour with Br or $C(NO_2)_4$ in $CHCl_3$. (III) is converted by $AlCl_3$ at room temp. into an *isomeride*, b.p. 90°/1·7 mm. The reactions of (I) and (II) with *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ are described. (I) does not appear to be reduced by Na and EtOH. (I) reacts partly with $(:CH{\cdot}CO)_2O$ giving a product identical with that described previously. (II) is oxidised by H_2O_2 in Ac_2O–H_2SO_4 to *oxidocaryophyllene*, b.p. 120°/3 mm., α_D −53·48°, and a resin. SeO_2 in boiling dioxan oxidises (II) to a mixture of di- and tri-cyclic dihydrosesquiterpenes, dihydrocaryophyllenal [*semicarbazone* (IV), m.p. 227—228°; 2 : 4-*dinitrophenylhydrazone*, m.p. 145—146° and 165—165·5° after resolidification], oxidised by Ag_2O to an acid, and dihydrocaryophyllenone [*semicarbazone* (V), m.p. 241—242°, $[\alpha]_D$ +67·50° in AcOH; 2 : 4-*dinitrophenylhydrazone*, m.p. 163—164°]. Ozonolysis of (II) gives inconclusive results. Treatment of (I), (II), (IV), or (V) with O_3 according to Dœuvre gives CH_2O only in case of (I); $COMe_2$ could not be detected. H. W.

Sesquiterpenes. XLIX. Additive product of maleic anhydride and caryophyllene. L. Ruzicka, P. A. Plattner, and G. Balla (*Helv. Chim. Acta*, 1941, **24**, 1219—1235; cf. A., 1935, 351).—The adduct (I) obtained by treating the caryophyllene (II) mixture with $(:CH{\cdot}CO)_2O$ is the anhydride of a doubly unsaturated dicyclic dicarboxylic acid. It appears to be the result of a normal diene addition to a relatively strongly lævorotatory monocyclic sesquiterpene in which a non-conjugated arrangement of two double linkings has been transformed into a conjugated form. All conclusions with regard to the constitution of the dicyclic sesquiterpene which gives degradation products of the (II) type which are based on the existence and properties of (I) are withdrawn. Different samples of (II) react very differently with $(:CH{\cdot}CO)_2O$, the power of forming an adduct appearing to be independent of b.p., *d*, or *n* but to increase with increasing lævorotatory power of the hydrocarbon. Samples giving good yields of (I) appear to yield the known dihydrochloride in small amount. Treatment of (II) with $(:CH{\cdot}CO)_2O$ appears to lead to great enrichment of the residue in the substance which reacts with HCl. (I), m.p. 98°, $[\alpha]_D$ +28° in EtOH, +49° in $CHCl_3$, gives a distinct yellow colour with $C(NO_2)_4$. Protracted boiling of (I) with H_2O or, preferably, shorter treatment with dil. HCl converts (I) into the lactonic *acid* (III), $C_{19}H_{28}O_4$ (previously "dicarboxylic acid"), m.p. 208°, $[\alpha]_D$ −32·0° in 1·5% KOH, which does not give a colour with $C(NO_2)_4$. (III) and CH_2N_2 give the corresponding *Me* ester (IV), m.p. 156°, hydrolysed to the *hydroxydicarboxylic* acid, $C_{19}H_{30}O_5$, m.p. ~160° (decomp.) with production of (III) at a somewhat higher temp. (I) is converted by 2N-Na_2CO_3 at 100° followed by cautious treatment with AcOH into the non-cryst. dicarboxylic acid, $C_{19}H_{28}O_4$, converted by warm Ac_2O into (I) and by CH_2N_2 into the Me_2 ester, b.p. ~150°/1 mm., $[\alpha]_D$ +32° in EtOH. (I) and boiling, saturated HCl–MeOH yield the Me_2 ester, $C_{21}H_{32}O_4$, b.p. 165°/1 mm., also obtained from (III) and (IV), which does not appear to be quite homogeneous; when hydrolysed it gives an *acid*, $C_{19}H_{28}O_4$, m.p. 173°, $[\alpha]_D$ −217° in EtOH, which is unsaturated towards $C(NO_2)_4$ and does not regenerate (I) when boiled with Ac_2O, together with non-cryst. material of lower $[\alpha]$. Hydrogenation of (I) in presence of Raney Ni causes absorption of 2 H but the product, the acid obtained therefrom, and its Me_2 ester are non-cryst. and, unexpectedly, strongly unsaturated towards $C(NO_2)_4$. In presence of PtO_2 there is absorption of 4 H; the saturated anhydride is hydrolysed to the *cis*-tetrahydro-acid [Me_2 ester (V), b.p. 160°/1 mm.; $[\alpha]_D$ −18° in EtOH]. (V) is converted into the corresponding *dianilide*, m.p. 222° (vac.), and by NaOEt–EtOH into the trans-Me_2 ester, b.p. 160°/1 mm., $[\alpha]_D$ +0·9° in EtOH [corresponding *dianilide*, m.p. 229° (vac.), $[\alpha]_D$ +44° in $COMe_2$]. $(:C{\cdot}CO_2Me)_2$ and a sample of (II) yield an adduct, hydrolysed to an *acid*, $C_{19}H_{26}O_4$, m.p. 120°. M.p. are corr. H. W.

Diterpenes. XLVIII. Degradation of agathenedicarboxylic acid with potassium permanganate. L. Ruzicka and E. Bernold (*Helv. Chim. Acta*, 1941, **24**, 931—939).—Agathenedicarboxylic acid (I) is oxidised by $KMnO_4$ and the acid degradation products are esterified by HCl–MeOH, whereby only a part of the acids is completely esterified. The resulting non-separable mixture of esters is hydrolysed to a non-separable mixture of acids. Esterification of the less reactive acids is completed by CH_2N_2 and the resulting esters yield a fraction, b.p. 127—128°/0·2 mm., $[\alpha]_D$ +41° in MeOH, which appears to be the Me_3 ester of an acid, $C_{12}H_{18}O_6$ (II). This is hydrolysed by saturated HBr at 0° to the *substance* (III), $C_{12}H_{16}O_5$, m.p. 103—104°, $[\alpha]_D$ +58° in $CHCl_3$, which is the anhydride of the Me_1 ester of (II). (III) could not be completely hydrolysed by very conc. alkali hydroxide. The difficultly hydrolysed ester group corresponds with the *tert.* CO_2H of (I). The anhydride is not identical with the similar product from abietic acid. A series of homologous esters, $C_{16}H_{24}O_7$, $C_{17}H_{26}O_7$, and $C_{18}H_{28}O_7$, appears to be present in the less volatile fractions of the difficultly formed esters; the presence of CO could not be established. M.p. are corr. H. W.

Diterpenes. L. Degradation of methyl *iso*noragathate with ozone. L. Ruzicka and E. Bernold (*Helv. Chim. Acta*, 1941, **24**, 1167—1178; cf. A., 1938, II, 371).—It is placed beyond doubt that acids with CO_2H in ring B are not present in the main portion of the mixture of isomeric monocarboxylic acids $C_{19}H_{30}O_2$ known as *iso*noragathic acid. As assumed previously, decarboxylation of *iso*agathendiacid involves the elimination of *tert.* CO_2H in ring A. Ozonisation of Me *iso*noragathate, m.p. 108—109° (*loc. cit.*), shows it to be non-homogeneous and yields a *ketodicarboxylic ester* (I), m.p. 103—104°,

$[\alpha]_D^{20}$ −15·03° in $CHCl_3$, a *tricarboxylic ester*, $C_{21}H_{34}O_6$, b.p. 160—162°/0·2 mm., the Me_1 ester of a ketodicarboxylic acid, $C_{20}H_{32}O_3$ (**II**), m.p. 174—175°, $[\alpha]_D^{20}$ −9·37° in $CHCl_3$, which passes into (**I**) when treated with CH_2N_2, and the Me_1 ester of an isomeric ketodicarboxylic acid (**III**), m.p. 159—160°, $[\alpha]_D^{20}$ +1·41° in $CHCl_3$ (corresponding Me_2 ester, m.p. 70—71°, $[\alpha]_D^{20}$ +17·36° in $CHCl_3$). Oxidation of (**II**) with Br–KOH gives the Me_1 ester of a tricarboxylic acid, $C_{19}H_{30}O_6$ (**IV**), m.p. 229—230°, $[\alpha]_D^{20}$ +5·07° in aq. NaOH, and of (**III**) gives an isomeric *substance*, m.p. 167—168°. Boiling Ac_2O dehydrates (**IV**) to an *anhydride*, $C_{19}H_{28}O_5$, m.p. 206—208°, $[\alpha]_D^{20}$ +6·04° in $CHCl_3$, which passes at ~230°/vac. into the *ketone*, $C_{18}H_{28}O_3$, m.p. 144—145°, $[\alpha]_D^{20}$ +173·42° in $CHCl_3$. *iso*Noragathenol, m.p. 115—116°, is converted (Ac_2O in abs. C_5H_5N at 100°) into its *acetate*, b.p. 151—153°/0·3 mm., oxidised by SeO_2 in boiling C_6H_6 and subsequently with $Al(OPh)_3$ and $COMe_2$ to an $\alpha\beta$-unsaturated *ketone*, m.p. 103—104°. Agathendiacid at 240—250°/11 mm. is transformed into a variety of products of which *two*, $C_{19}H_{30}O_2$, m.p. 138—139°, $[\alpha]_D^{20}$ +50·63° in $CHCl_3$, and m.p. 107—108°, $[\alpha]_D^{20}$ +60·77° in $CHCl_3$, are isolated. M.p. are corr.

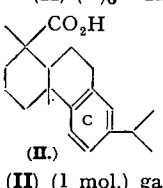
H. W.

Constitution of cafesterol. II. A. Wettstein and K. Miescher (*Helv. Chim. Acta*, 1942, **25**, 718—731; cf. A., 1942, II, 198).—Cafesterol (**I**) probably belongs to the diterpene series. Isolation of norcafestanolone-*B* (**II**), OH·C*H<$C_{16}H_{24}$>CHMe, m.p. 192—193° (acetate, m.p. 175—176°; no digitonide), by successive hydrogenation, hydrolysis, and oxidation (HIO_4) of cafesteryl acetate (**III**) is described; chromatography of the mixed products and treatment with $(CH_2{\cdot}CO_2)_2O$ etc. yields *norcafestanolone*-C (**IV**), CH_2<$C_{16}H_{24}O$>CH·CH_2·OH, m.p. 99—100° {*acetate*, m.p. 144—145° [2 : 4-*dinitrophenylhydrazone*, m.p. 242—243° (decomp.)]; no digitonide}. (**II**) and the *A*-compound are isomeric at C*, since with CrO_3 they yield the same norcafestanedione (**V**), m.p. 140—141°. The primary character of the OH of (**IV**) is proved by ready interaction with *o*-$C_6H_4(CO)_2O$ and oxidation by CrO_3–AcOH at room temp. to *norcafestanonic acid* (**VI**), CH_2<$C_{16}H_{24}O$>CH·CO_2H, *forms*, m.p. 161—162° and 198—199° [*Me*, m.p. 113—114° (2 : 4-*dinitrophenylhydrazone*, m.p. 230—232°), and *Et* ester, m.p. 122—123°, formed by CH_2N_2 or HCl–ROH at 0° and readily hydrolysed]. It follows that (**I**) contains the "*ox*-"O as >C*H·O·CH_2·CH< and that the ·CH_2·O· of (**VI**) and thus the –CH·CH_2·OH of (**IV**) is not sterically hindered. Less prolonged oxidation of (**IV**) gives *norcafestanonal*, CH_2<$C_{16}H_{24}O$>CH·CHO, m.p. 109—111° [reduces $AgNO_3$–NH_3–H_2O; gives a red colour with 1 : 4-$C_{10}H_6(OH)_2$–HCl–AcOH], the impure *disemicarbazone*, decomp. 330—400°, of which yields (Wolff–Kishner) norcafestane-*B* (? impure), m.p. 36°. Use of CrO_3–AcOH in place of HIO_4 in treatment of (**III**) as above gives much (**V**), some (**II**), *norcafestanolonolactone* A (**VII**), $C_{16}H_{24}O$<CH—CH·CO>O, m.p. 279—281° [2 : 4-*dinitrophenylhydrazone*, m.p. 288—289° (decomp.)], and (**VI**). (**VII**) is also obtained in poor yield from oxnorcafestanone *A*; oxnorcafestanone *B* gives a little (impure) *norcafestanolonolactone* B, m.p. 229—230°. M.p. are corr.

R. S. C.

Vetivones. Y. R. Naves (*Helv. Chim. Acta*, 1942, **25**, 698—699).—Concerning priority. R. S. C.

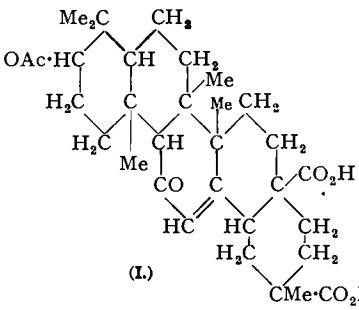
Dehydroabietic acid, $C_{20}H_{29}O_2$. R. Lombard (*Compt. rend.*, 1941, **213**, 793—796; cf. A., 1939, II, 334).—Abietic acid (**I**) (1 mol.) and S (1 mol.) at 180—230° give dehydroabietic acid (**II**) [identical with (**II**) from pyroabietic acid and from (**I**) and SeO_2]. Hydrogenation of (**II**) (2% Adams Pt, Pr^{β}_2O, 190°/100 kg.) yields a H_6-*acid*, $[\alpha]_{5780}$ +41°, whereas (**I**) affords a mixture of H_4-*acids*. Hydrogenation of (**I**) (Pd–C, 250°/100 kg.) affords a H_2-*acid*, $[\alpha]_{5780}$ +121°; (**II**) is unchanged. Four other examples are given of the lessened reactivity of the double linkings of (**II**). (**I**) (1 mol.) and 2—4% $KMnO_4$, then 1·4—1·5% HNO_2 (1% V_2O_5), yield 10 g. of non-aromatic acid, m.p. 235° [solidifies and remelts 280° (sublimes)], equiv. 79, [α] 0.

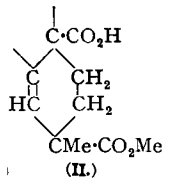


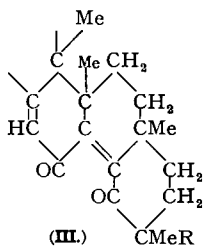
(II.)

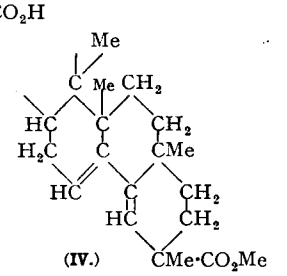
(**II**) (1 mol.) gave 15 g. of 1 : 2 : 4-$C_6H_3(CO_2H)_3$, m.p. 232° (amide m.p. 263°), which can only be formed from ring c. Rotation solvents not named. C. S.

Triterpenes. LXVII. Position of the carboxyl group in glycyrrhetic acid. L. Ruzicka and O. Jeger (*Helv. Chim. Acta*, 1942, **25**, 775—785).—The following and earlier data indicate (**I**) as most probable formula for glycyrrhetic acid. Its Me ester acetate with Br–AcOH–HBr (trace) gives *Me dehydroglycyrrhetate acetate* (**II**), m.p. 247—248°, $[\alpha]_D$ +282° in $CHCl_3$ (absorption max. 280 mμ., log ε 4·0), hydrolysed by boiling KOH–MeOH to the corresponding *acid*, m.p. ~215—220° (decomp.) [with CH_2N_2 regenerates (**II**)], which at ~205—210°/high vac. gives CO_2 and, by shift of an ethylenic linking, a *compound*, $C_{31}H_{46}O_3$, m.p. 164—165° (block), $[\alpha]_D$ −139° in $CHCl_3$ (absorption max. 235 mμ., log ε 4·35), very sensitive to SeO_2. With SeO_2 in dioxan at 200°, (**II**) gives *Me β-amyradienedionolate acetate* (**III**) (R = CO_2Me), $C_{33}H_{46}O_6$, m.p. 236—237°, $[\alpha]_D$ −73° in $CHCl_3$ (absorption max. 280 mμ., log ε 4·1), but in boiling AcOH gives also *Me dehydrodeoxoglycyrrhetate acetate* (**IV**), m.p. 232—233°. Boiling HCl–MeOH hydrolyses (**III**) (R = CO_2Me) to *Me β-amyradienedionolate*, m.p. 310—311°, $[\alpha]_D$ −96° in $CHCl_3$ [with Ac_2O–C_5H_5N regenerates (**III**) (R = CO_2Me)], but


(I.)


(II.)

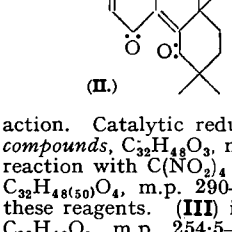

(III.)


(IV.)

boiling KOH–MeOH gives, by hydrolysis and loss of CO_2, *nor-β-amyradienedionol* (**III**) (R = H), m.p. 255—256°, $[\alpha]_D$ −36° in $CHCl_3$ [*acetate* (**V**), m.p. 279—280°], and (**III**) (R = CO_2H). (**III**) (R = H) with N_2H_4 gives the *pyridazine* derivative (free OH), m.p. 220—222° (absorption max. 280 mμ., log ε 4·2; *acetate*, m.p. 214—216°). Decarboxylation of (**III**) (R = CO_2H) in boiling xylene and subsequent acetylation gives (**IV**), m.p. 280—281°. M.p. are corr. R. S. C.

Saponins. XIII. Thermal decomposition of oleanolic acid. S. Kuwada (*J. Pharm. Soc. Japan*, 1936, **56**, 469—478; cf. A., 1937, II, 512).—Thermal decomp. of oleanolic acid gives *oleanylene* (**I**), m.p. 185—186°, *oleanol* (**II**) (*acetate*, m.p. 210—211°), and a *hydrocarbon*, $C_{28}H_{46}$, m.p. 164—166°. (**I**) is reduced catalytically to *dihydro-oleanylene*, m.p. 194°, and *dihydro*iso*oleanylene* (**III**), m.p. 219—220°, and by the Clemmensen method to iso*oleanylene*, m.p. 183—185°. (**II**) is oxidised (CrO_3) to *oleanolone*, m.p. 172°, and this reduced to (**III**). CH. ABS. (*c*)

Triterpenes. LXII. Introduction of double linkings and carbonyl groups into the rings C—E of β-amyrin. L. Ruzicka and O. Jeger (*Helv. Chim. Acta*, 1941, **24**, 1236—1248).—Oxidation of β-amyrin acetate with SeO_2 in boiling AcOH gives dehydro-β-amyrin acetate [β-amyradienol II acetate] (**I**), m.p. 228—229°, and the compound [(**II**) R = Ac], m.p. 234—235°, identical with the substance of Jacobs and Fleck (A., 1930, 1292). (**II**) is hydrolysed by acid or alkali to the *compound* (**III**), $C_{30}H_{44}O_3$ [(**I**) R = H], m.p. 290—291°, and is transformed by N_2H_4,H_2O in EtOH at 200° into the *pyridazine* derivative, $C_{30}H_{44}ON_2$, m.p. 292—293°, which gives a pronounced brown colour with $C(NO_2)_4$, can be sublimed at 205—210°/high vac., and does not undergo the Wolff–Kishner reaction.

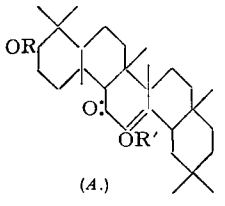


(II.)

Catalytic reduction (Pt-black in AcOH) of (**II**) gives two *compounds*, $C_{32}H_{48}O_3$, m.p. 197—199°, which gives a strong positive reaction with $C(NO_2)_4$ and a blood-red colour in conc. H_2SO_4, and $C_{32}H_{48(50)}O_4$, m.p. 290—292°, which does not give a colour with these reagents. (**III**) is reduced (PtO_2 in AcOH) to the *substance*, $C_{30}H_{48}O_2$, m.p. 254·5—246° (*acetate*, m.p. 219—219·5°). Hydrogenation (PtO_2 in AcOH) of (**I**) yields a new isomeric *amyrin acetate*, m.p. 208·5—209·5°, $[\alpha]_D$ −35° in $CHCl_3$, hydrolysed to an isomeric *amyrin*, m.p. 213—213·5°, $[\alpha]_D$ −52° in $CHCl_3$ (*benzoate*, m.p. 224—225°, $[\alpha]_D$ −8° in $CHCl_3$). Oxidation (CrO_3 in AcOH) of (**I**) gives a *compound*, $C_{32}H_{46}O_5$, m.p. 256—256·5°. M.p. are corr. H. W.

Triterpenes. LXI. Conversion of β-amyranolone into β-amyran and into enol-β-amyranoldione. L. Ruzicka and O. Jeger (*Helv. Chim. Acta*, 1941, **24**, 1178—1189).—The CO group of β-amyranolone (Picard *et al.*, A., 1939, II, 121; Ruzicka *et al.*, *ibid.*, 330) is identified by hydrogenation (PtO_2 in AcOH) followed immediately by loss of H_2O to β-amyrin, m.p. 188—189° (acetate, m.p. 241—242°), whilst β-amyranolone acetate (**I**), m.p. 291—292°, is transformed by N_2H_4,H_2O in EtOH at 200° into *β-amyranolonehydrazone* (+1MeOH), m.p. 138·5—139·5°. (**I**) is reduced (Wolff–Kishner) to *β-amyranol*, m.p. 186—186·5°, $[\alpha]_D$ +18·4° in $CHCl_3$ (*acetate*, m.p. 284·5—285°, $[\alpha]_D$ +21° in $CHCl_3$), oxidised (CrO_3 in AcOH) to *β-amyranone*, m.p. 194—195° [*semicarbazone*, m.p. 234—236° (decomp.)]; this is converted by NaOEt and N_2H_4,H_2O in EtOH at 200° into *β-amyran*,

m.p. 172—173°, $[\alpha]_D$ +9·9° in $CHCl_3$. (**I**) is oxidised by SeO_2 in dioxan at 190—200° to *enol-β-amyranoldione acetate* (**II**) (*A*; R = Ac; R′ = H), m.p. 262—263°, $[\alpha]_D$ +116° in $CHCl_3$, which gives a pale yellow colour with $C(NO_2)_4$ and a green colour with $FeCl_3$ in dioxan but not in Et_2O or EtOH; it is converted by Ac_2O–C_5H_5N into the *diacetate* (**III**), m.p. 232°, $[\alpha]_D$ +77·5° in $CHCl_3$, and hydrolysed by KOH–MeOH to *enol-β-amyranoldione* (**IV**) (*A*; R = R′ = H), m.p. 222—223°, $[\alpha]_D$ +136·5° in $CHCl_3$, which does not appear to yield a quinoxaline derivative. (**III**) is hydrolysed and then reduced by Na and boiling EtOH to β-amyrandiolone isolated (after acetylation) as the monoacetate, m.p. 299—300°, which is oxidised by CrO_3 in AcOH to (**II**). (**I**) is transformed by NaOAc and boiling Ac_2O into *enol-β-amyranolone diacetate*, m.p. 233—234°, which with CrO_3 and H_2SO_4 yields *enol-β-amyranoldione diacetate*, m.p. 233°, hydrolysed by alkali to (**IV**). M.p. are corr. H. W.


(*A*.)

Synthesis of 5-hydroxy-1 : 6-dimethyl-4-*iso*propylnaphthalene, a contribution to the elucidation of the constitution of guaiol.—See A., 1942, II, 356.

Interaction of amines with nitrous acid.—See A., 1942, II, 359.

γ-Diketones.—See A., 1942, II, 363.

VI.—HETEROCYCLIC.

Furancarboxylic acid derivatives.—See B., 1942, II, 315.

***O*-Furoylsalicylic acid.**—See B., 1942, III, 223.

Isosteric and structurally similar compounds. XIII. Furyl*iso*propylamine and other amines of the furan series. H. Erlenmeyer and M. Simon (*Helv. Chim. Acta*, 1941, **24**, 1210—1213).—2-Furonitrile is treated successively with MgEtBr and EtOH and the product is reduced by Na and boiling EtOH to 2-*α-amino*-n-*propylfuran*, b.p. 83—85°/14 mm. (*picrate*, m.p. 168°; *picrolonate*, m.p. 185°). Furylacetone is converted into the *oxime*, b.p. 113—115°/15 mm., m.p. 19—20°, which is reduced (Na and EtOH) to 2-*β-amino*-n-*propylfuran*, b.p. 66—68°/21 mm., 131—132°/758 mm. (*picrate*, m.p. 160°; hygroscopic *hydrochloride*). Similarly furfurylacetone affords the *oxime*, b.p. 136—137°/120 mm., and thence 2-*γ-amino*-n-*butylfuran*, b.p. 78°/90 mm. (*hydrochloride*). H. W.

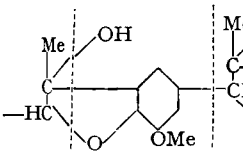
Action of formaldehyde on ethyl pyromucate. Resins of the furan series. II. D. Dinelli and G. B. Marini-Bettòlo (*Gazzetta*, 1941, **71**, 117—128).—Et pyromucate (**I**) and $(CH_2O)_3$ (**II**) in conc. H_2SO_4 give a resin (*A*) and 5 : 5′-dicarbethoxydifurfurylmethane (**III**). With excess of (**II**), (**I**) gives a resin (*B*). With paraformaldehyde (**IV**), (**I**) gives a resin (*C*) (cf. A., 1937, II, 513) containing CO_2Et residues attached to a chain of furan groups united by $\cdot CH_2\cdot O\cdot CH_2\cdot$ and $\cdot CH_2\cdot$ groups. *A*, *B*, and *C* are sol. in org. solvents. At 220°, *C* loses CH_2O and gives a less sol. resin. With NaOH in aq. EtOH, *C* gives an acid resin, which when heated loses CO_2. Similar products are obtained from (**III**) and (**IV**), or from Me pyromucate, in conc. H_2SO_4. Furfuryl alcohol with 0·02% of $HgCl_2$ (**V**) at 80° [or spontaneously and violently with large proportions of (**V**)] gives a resin. 5-Methylfurfuraldehyde is hydrogenated (150—160 atm.; 150°; Cu chromite) to 5-methylfurfuryl alcohol; this is resinified by I, as are its *acetate*, b.p. 96°/16 mm., and its *Me*, b.p. 70—75°/32 mm., and *Et ether*, b.p. 65—68°/12 mm. E. W. W.

Raman effect and problems of constitution. XIX. 2 : 6-Dimethyl-4-pyrone. L. Kahovec and K. W. F. Kohlrausch (*Ber.*, 1942, **75**, [*B*], 627—632; cf. Volkenstein *et al.*, A., 1939, I, 597).—Clear evidence of the existence of mesomerism in 2 : 6-dimethyl-4-pyrone (**I**) cannot at present be deduced from the Raman spectrum. If mesomerism be assumed a more or less convincing explanation is readily found for certain spectral anomalies which result when (**I**) passes into its hydrochloride. It cannot be shown that this is the only possible explanation. H. W.

1 : 4-Pyrones.—See B., 1942, II, 362.

Orientation in the coumaran series. R. T. Arnold and J. C. McCool (*J. Amer. Chem. Soc.*, 1942, **64**, 1315—1317).—1-Methylcoumaran, Ac_2O, and $AlCl_3$ in $PhNO_2$ at >10° give 4-aceto-1-methylcoumaran (**I**), b.p. 145—146°/6 mm., the structure of which is proved by conversion of its *oxime*, m.p. 85—86°, by HCl–Ac_2O–AcOH into 4-acetamido-1-methylcoumaran (**II**), m.p. 127—128° (and thence the amine hydrochloride), and by synthesis as follows: heating *p*-allyloxyacetophenone (prep. from *p*-OH·C_6H_4·COMe, CH_2:CH·CH_2Br, and K_2CO_3 in $COMe_2$), b.p. 146—147°/10 mm. (*oxime*, m.p. 115·5—116·5°), at 200—210° (CO_2) gives 3 : 4 : 1-CH_2:CH·CH_2·C_6H_3(OH)·COMe, m.p. 115—116°, which with boiling 40% aq. HBr–AcOH gives (**I**). HNO_3 (*d* 1·5) and (**II**) in AcOH give 3-*nitro*-4-*acetamido*-, m.p. 135—136°, and thence (boiling 1 : 1 conc. HCl–H_2O) 3-*nitro*-4-*amino*- (40%), m.p. 104—104·5°, and (diazo-reaction; $CuSO_4$) 3-*nitro*- (**III**), m.p. 67·5—68°, 1-*methylcoumaran*. Fe–AcOH–H_2O and then Ac_2O converts (**III**) into 3-acetamido-1-methylcoumaran, m.p. 96—97°. 4 : 3 : 1-CH_2:CH·CH_2·C_6H_3(OH)·NHAc and fuming HBr at room temp. give 5-*acetamido*-1-*methylcoumaran*, m.p. 126—126·5°. 4 : 3 : 1-OMe·C_6H_3Me·NHAc and HNO_3–AcOH at 10—20° give *acet*-6-*nitro*-4-*methoxy*-m-*toluidide*, m.p. 144°, the structure of which is proved by hydrolysis to 6-*nitro*-4-*methoxy*-m-*toluidine*, m.p. 117·5—118·5°, the diazonium salt of which with 1 : 5-$C_{10}H_6(SO_3Na)_2$–H_2SO_4–H_2O and then Cu powder in EtOH gives 4 : 1 : 2-NO_2·C_6H_3Me·OMe, m.p. 71·5—72·5° (lit. 71°), or with $CuSO_4$ gives 6-*nitro*-4-*methoxy*-m-*cresol*, m.p. 98—99°. R. S. C.

Occurrence of substituted cumarones (benzfurans) in beech wood tar, and their relation to lignin. A. von Wacek and E. Nittner (*Cellulose-Chem.*, 1940, 29—33; *Canad. Pulp and Paper Assoc.*, 1941).—Decomp. of beech wood tar with O_3 yields an acidic, a neutral, and a phenolic fraction. The first contains 3- and 4-methylsalicylic acids, thereby proving the occurrence of 1-substituted 5- and 6-methylbenzfuran. From one fraction (b.p. 88—91°/9 mm.) of the neutral oil an alkali-sol. mixture of OH-acids and OH-aldehydes was obtained in 40% yield by fission. A fraction, b.p. 132—135°/15 mm., had a relatively high OMe content, indicating the presence of methoxylated benzfurans, and also yielded after fission a methoxy-methylsalicylic acid which must have been formed from a methoxybenzfuran (**I**) (possibly 2-substituted). These results prove that the benzfurans originated in the lignin (**II**) of the beech wood, and also verify Freudenberg's theory that (**II**) contains a C–C condensation product in the *o*-position to a bridge chain. This theory, however, does not account for the presence of (**I**), which could be accounted for by the annexed scheme. H. A. H.



Crystalline natural α-tocopheryl acetate. C. D. Robeson (*J. Amer. Chem. Soc.*, 1942, **64**, 1487).—"Natural" α-tocopheryl acetate is obtained from MeOH at −30° and then from HCO_2Me at −30°, having m.p. 26·5—27·5°, $E^{1\%}_{1cm.}$ (286 mμ.) 41·2, and giving α-tocopherol (99·4% pure), $E^{1\%}_{1cm.}$ (292 mμ.) 73·8. R. S. C.

Phenol–formaldehyde resins. I. Reaction of phenolic alcohols with unsaturated substances. K. Hultzsch (*J. pr. Chem.*, 1941, [ii], **158**, 275—294).—*o*-Hydroxybenzyl alcohols and many (not all) unsaturated compounds give heterocyclic products. ArOH and CH_2O–NaOH–H_2O give 2-*hydroxy*-3-*methyl*-5-tert.-*butyl*- (**I**), m.p. 64°, and -5-cyclo*hexyl*-3-*methyl*-*benzyl alcohol* (**II**), m.p. 78°. Heating *o*-OH·C_6H_4·CH_2·OH with CHPh:CH_2 (excess) with removal of H_2O gives 2-phenylchroman. 2 : 3 : 5 : 1-OH·$C_6H_2Me_2$·CH_2·OH (**III**) with CHPh:CH_2 and indene give 2-phenyl-6 : 8-dimethylchroman, b.p. 195°/14 mm., and 6 : 8-dimethyl-2 : 3-hydrindochroman, b.p. 205°/14 mm., respectively. CHMe:CH·CO_2H with (**I**) or (**II**) at 200° gives 3(or 2) : 8-*dimethyl*-6-tert.-*butyl*-, m.p. 164°, or -6-cyclo*hexyl*-*chroman*-2(or 3)-*carboxylic acid*, m.p. 158°, respectively. Et_2 maleate (**IV**) and (**I**) at 220° give, after hydrolysis (33% NaOH), 8-*methyl*-6-tert.-*butylchroman*-trans-2 : 3-*dicarboxylic acid* (**V**), m.p. 245°, converted by way of the oily anhydride into the *cis*-isomeride, m.p. 222°, whence EtOH–H_2SO_4, then NaOMe, and hydrolysis regenerate (**V**). 2 : 5 : 1-OH·C_6H_3Me·CH_2·OH and (**IV**) at 270° give similarly 6-*methylchroman*-2 : 3-*dicarboxylic acid*, m.p. 247·5° (and some phenolic aldehyde; cf. A., 1939, II, 209), but 1 : 4 : 2 : 6-OH·$C_6H_2Me(CH_2·OH)_2$ gives a mixture. (2 : 3 : 5 : 1-OH·$C_6H_2Me_2)_2O$ and (**IV**) give an oil, b.p. 200—240°/vac., converted by hydrolysis into 6 : 8-*dimethylchroman*-2 : 3-*dicarboxylic acid* (mixed isomerides), m.p. 220—235°. *n*-C_5H_{11}·CO·O·CH_2·CH:CH_2 and (**III**) at 220° give a solid product, hydrolysed to 6 : 8-*dimethyl*-2(or 3)-*hydroxymethylchroman*, m.p. 96°. α-Terpineol with (**III**), oleic and abietic acid with (**I**) give oily condensation products. $CH_2Ac·CO_2Et$ and (**III**) at 200° give *Et* 3(or 2) : 6 : 8-*trimethylbenzopyran*-2(or 3)-*carboxylate*, m.p. 75·5°, and thence the *acid*, m.p. 230—235° (decomp.), both resistant to hydrogenation. CPh:C·CO_2Et and (**III**) at 200—250° give exothermally an oil, hydrolysed to 2(or 3)-*phenyl*-6 : 8-*dimethylbenzopyran*-3(or 2)-*carboxylic acid*, m.p. 205—208° (decomp.). Attempted condensations which failed are listed. 1 : 4 : 2 : 6-CH_2Ph·O·$C_6H_2Me(CH_2·OH)_2$ has m.p. 111·5°. R. S. C.

New general method for synthesising coumarins. L. Bert (*Compt. rend.*, 1942, **214**, 230—232).—PhOR and $CH_2Cl·CH:CHCl$ (**I**) ($AlCl_3$ or Zn dust) or *o*-C_6H_4(MgBr)·OR and (**I**) yield *o*-RO·C_6H_4·CH_2·CH:CH·CH_2·OR′, converted by conc. HCl (100°, autoclave) into *o*-RO·C_6H_3·CH:CH·CH_2Cl. $(CH_2)_6N_4$ in a "hydro-alcohol" on this yields the aldehyde (**III**), atm. oxidation of which gives the acid, hydrolysed (conc. HBr) with ring-closure to coumarin. (**II**) and Br–$CHCl_3$ at 0° give a Br_2-compound which with NaOEt yields an acetal, hydrolysed (HCl, ¼ hr.) to (**III**). Umbelliferone, herniarin, and æsculetin have also been prepared. W. C. J. R.

Pechmann condensation of phenols with ethyl butyroacetate. N. G. Kotwani, S. M. Sethna, and G. D. Advani (*Proc. Indian*

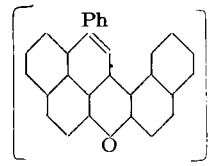
Acad. Sci., 1942, **15**, **A**, 441—444).—Et butyroacetate (**I**), *m*-$C_6H_4(OH)_2$, and 75% H_2SO_4 at room temp. give 7-*hydroxy*-4-*propylcoumarin*, m.p. 130° (*acetate*, m.p. 118—119°; *Me ether*, m.p. 145—146°), converted by Me_2SO_4–aq. NaOH–$COMe_2$ into 2 : 4-*dimethoxy*-β-*propylcinnamic acid*, m.p. 83—85°. Orcinol similarly yields 5-*hydroxy*-7-*methyl*-4-*propylcoumarin*, m.p. 180° (*acetate*, m.p. 120—121°; *Me ether*, m.p. 78—79°), and thence 2 : 6-*dimethoxy*-4-*methyl*-β-*propylcinnamic acid*, m.p. 165°. 1 : 2 : 3- or *s*-$C_6H_3(OH)_3$ afford 7 : 8-*dihydroxy*-, m.p. 198—200° (*diacetate*, m.p. 150—152°; *Me*$_2$ *ether*, m.p. 95°), or 5 : 7-*dihydroxy*-4-*propylcoumarin*, m.p. 258° (*diacetate*, m.p. 145°; *Me*$_2$ *ether*, m.p. 150°), respectively, and thence 2 : 3 : 4-, m.p. 134—136°, or 2 : 4 : 6-*trimethoxy*-β-*propylcinnamic acid*, m.p. 140°, respectively. α-$C_{10}H_7$·OH gives α-*naphtho*-4-*propyl*-α-*pyrone*, m.p. 108—110°. PhOH, cresol, quinol, β-$C_{10}H_7$·OH, 2 : 4 : 1-$(OH)_2C_6H_3$·CO_2Me, or 2 : 4 : 1-$(OH)_2C_6H_3$·COMe does not condense with (**I**) in presence of P_2O_5, $POCl_3$, $AlCl_3$, or H_2SO_4. A. T. P.

Chemotherapy of bacterial infections. VI. Synthesis of N^1-substituted sulphanilamides; poly- and hetero-cyclic derivatives. S. Rajagopalan and K. Ganapathi (*Proc. Indian Acad. Sci.*, 1942, **15**, **A**, 432—436; cf. A., 1941, II, 338).—*p*-NHAc·C_6H_4·SO_2Cl and the respective amine in C_5H_5N, followed by hydrolysis of the Ac derivative, give: 2-, m.p. 149° (*Ac* derivative, m.p. 162°), and 4-*sulphanilamidodiphenyl ether*, m.p. 177—178° (*Ac* derivative, m.p. 183°), 3-*sulphanilamidophenanthrene*, m.p. 213—215° (*Ac* derivative, m.p. 244—245°), 6-*sulphanilamidochrysene*, m.p. 265°, 9-*sulphanilamidocarbazole*, m.p. 224° (decomp.) [*Ac* derivative, m.p. 202—203° (decomp.)], 6-*sulphanilamidocoumarin*, m.p. 189—190°, 9-sulphanilamidoacridine [*dihydrochloride*; *Ac* derivative, m.p. 273—275° (decomp.)], 6 : 7-*dimethoxy*-1-p-*sulphanilamidophenyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m.p. 162° (sinters at 159°), 9-m-*sulphanilamidophenylphenanthridine*, m.p. 251—253° (sinters at 246°), and 4-*aminonaphthalene*(?-1-)*sulphonamide*, m.p. 250—251° (decomp.).

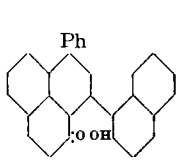
o-C_6H_4Ph·NHAc and $ClSO_3H$ give a chloride, and thence 2-*aminodiphenyl*-5(?)-*sulphonamide*, m.p. 185° (sinters at 183°). *p*-NH_2·C_6H_4·OPh [hydrochloride, new m.p. 225—227° (decomp.)] is prepared from the Ac derivative, new m.p. 130°, obtained by Beckmann rearrangement (HCl–Ac_2O–AcOH at 0°) of *p*-OPh·C_6H_4·CMe:N·OH. 3 : 4 : 1-$(OMe)_2C_6H_3$·$[CH_2]_2$·NH_2 gives p-*nitrobenzhomoveratrylamide*, m.p. 149°, converted ($POCl_3$) into 6 : 7-*dimethoxy*-1-p-*nitrophenyl*-3 : 4-*dihydro*isoquinoline, m.p. 158—159°, reduced by Zn–aq. H_2SO_4 at 100° (bath) to 6 : 7-*dimethoxy*-1-p-*aminophenyl* 1 : 2 : 3 : 4-*tetrahydro*isoquinoline, m.p. 151—153°. (*o*-OH·C_6H_4)$_2$ and $ZnCl_2$ at 230—250° affords dibenzofuran. A. T. P.

Quinone dye of the phenanthrofuran series. II. Constitution of tanshinone. I. F. von Wessely and A. Bauer (*Ber.*, 1942, **75**, [*B*], 617—625; cf. A., 1940, II, 286).—Tanshinone I (**I**) is hydrogenated (Pd sponge in EtOH) and then methylated (Me_2SO_4–NaOH at 50°) to *leucotanshinone Me*$_2$ *ether*, m.p. 94°, softens at 92·5° [*picrate*, m.p. 134° (Kofler)], ozonised and then degraded by boiling H_2O containing Zn dust and $AgNO_3$ or by Zn dust and AcOH to (mainly) 1-methylnaphthalene-5 : 6-dicarboxylic anhydride (**II**), m.p. 196°, and a cryst. yellow *compound* (**III**), $C_{19}H_{18}O_4$, m.p. 153° (Kofler) [*acetate*, m.p. 127°, softens at 125°; *Me ether*, b.p. 150—160°/0·05 Torr (picrate)]. (**II**) is very stable towards $KMnO_4$. Ozonisation appears complex and the structure of (**I**) cannot be deduced. Control experiments show that (**III**) is ozonised to (**II**) and that (**III**) is largely unchanged when added to the ozonides from coumarone and 2-methylcoumarone and then treated with Zn dust and AcOH. Ozonisation of BzAc gives immediately a small proportion of BzOH but the diketone appears largely unaffected during the reductive fission of coumarone ozonide. H. W.

Dehydrenium. V. Dehydrenium salts of the styrylxanthenium series. W. Dilthey, H. Stephan, and W. Oversohl (*Ber.*, 1942, **75**, [*B*], 675—686).—$(2\text{-}C_{10}H_7)_2O$ (**I**), CH_2Ph·CH_2·COCl (**II**), and sublimed $FeCl_3$ in boiling CS_2 afford *ms*-β-phenylethyl-1 : 2 : 7 : 8-dibenzoxanthenium chloride (as additive *salt* with $FeCl_3$), converted by boiling $COMe_2$–25% NH_3 into the non-cryst. *carbinol*, which is dehydrated by AcOH–Ac_2O to ms-*phenylethylidene*-1 : 2-7 : 8-*dibenzoxanthen* (**III**), m.p. 176—177° (*perchlorate*, m.p. 199—201°), also obtained by heating (**I**) and (**II**) with $ZnCl_2$. (**III**) is reduced by Zn dust and hot AcOH to ms-β-*phenylethyl*-1 : 2-7 : 8-*dibenzoxanthan* (**IV**), m.p. 171°, oxidised by PbO_2 in AcOH to (**III**) and the dibenzoxanthone (**V**), m.p. 193—194°. (**III**) and Br in AcOH afford ms-α-1-*bromo*-β-*phenylethylidene*-1 : 2-7 : 8-*dibenzoxanthen*, m.p. 164°, transformed by an excess of Br into the *perbromide*, $C_{29}H_{19}OBr_5$. (**I**), CHPh:CH·COCl, and $FeCl_3$ in CS_2 yield the double *salt*, $C_{29}H_{19}OFeCl_4$, converted by boiling $COMe_2$–25% NH_3 into ms-*styryl*-1 : 2-7 : 8-*dibromoxanthenol* (**VI**), which is reduced by Na and EtOH to (**IV**). (**VI**) and $HClO_4$ in AcOH yield the corresponding *perchlorate* (**VII**), m.p. 160° (decomp.), softens at 140°, also obtained from CHPh:CHBr, Mg, and (**V**) and transformed by Zn dust and cold AcOH containing conc. HCl into ms-*styryl*-1 : 2-7 : 8-*dibenzoxanthen*, m.p. 222—224° (decomp.). (**I**), CHPh:CH·COCl, and $ZnCl_2$ react when triturated and at 110—135° copious evolution of HCl occurs with formation of the $ZnCl_2$ double *salt* (**VIII**) of dehydro-*ms*-styryl-1 : 2-7 : 8-dibenzoxanthenium chloride (cf. *A*), also obtained from (**I**), (**II**), and $ZnCl_2$ but only in very poor



(*A*.)



(*B*.)

yield if the acids are used; it gives a corresponding *perchlorate* (**IX**), m.p. 272—273°. (**VIII**) is hydrolysed by dil. NH_3 to the perinaphthindenone *derivative* (*B*), m.p. 195—198° (decomp.), which gives a *Me ether*, m.p. 218° (*perchlorate*, m.p. ~160°; violent decomp. ~200°). Dehydrogenation of (**VII**) in $PhNO_2$ by sunlight yields (**IX**) and (**III**). *trans*-β-Chlorocinnamic acid, (**I**), and $FeCl_3$ in CS_2 afford the *salt*, $C_{29}H_{18}OClFeCl_4$, m.p. ~170° (decomp.), hydrolysed to ms-*chlorostyryl*-1 : 2-7 : 8-*dibenzoxanthenol*, m.p. 161—165° (slight decomp.) after becoming discoloured at ~135°, which with $HClO_4$ in warm AcOH in the dark gives ms-*chlorostyryl*-1 : 2-7 : 8-*dibenzoxanthenium perchlorate*, m.p. 160—170° (much decomp.), converted by irradiation in $PhNO_2$ into (**IX**). H. W.

Base-catalysed cleavage of methylenedioxy-rings. R. T. Arnold, N. Bortnick, and E. McMullen (*J. Amer. Chem. Soc.*, 1942, **64**, 1410—1413).—Relative amounts of *o*-$C_6H_4(OH)_2$ (**I**) (determined by NO_2'–molybdate) obtained by 20% KOH–EtOH (cf. Slooff, A., 1936, 838) are given in parentheses below prefixed by *c*. COMeR, (**I**), and P_2O_5 give 2-methyl-2-carbethoxymethyl- (50%), b.p. 146—148°/17 mm. (*c* 20·0), -2-α-*carbethoxyethyl*- (42%), b.p. 146—148°/17 mm. (*c* 71·0), -2-*acetonyl*- (16%), b.p. 136—138°/20 mm. (*c* 99·0), -2-α-*carbethoxy*isopropyl- (32%), b.p. 111—113°/5 mm. (*c* 0), and -2-β-*carbethoxyethyl*- (50%), b.p. 157—160°/17 mm. (*c* 0), giving by alkaline hydrolysis 2-methyl-2-carboxymethyl- (poor yield) (**II**), m.p. 61·5—62° (*c* 5·1), -2-α-*carbethoxyethyl*- (**III**) (poor yield), m.p. 89·5—90° (*c* 31·0), -2-α-*carboxy*isopropyl- (90%), m.p. 90—90·5°, and -2-β-*carboxyethyl*- (90%), m.p. 73—73·5°, -4 : 5-*benz*-1 : 3-*dioxole*, *o*-C_6H_4<O>CMeR. 4 : 1 : 2 -$C_6H_3Me(OH)_2$ gives similarly 2 : 4′-*dimethyl*-2-*carbethoxymethyl*- (41%), b.p. 157—159°/19 mm. (*c* 7·2), -2-α-*carbethoxyethyl* (37%), b.p. 162—164°/21 mm. (*c* 53·4), -2-α-*carbethoxy*isopropyl- (40%), b.p. 164—166°/21 mm. (*c* ? 4·5), and -2-β-*carbethoxyethyl*- (50%), b.p. 172—174°/19 mm. (*c* 0), and thence 2 : 4′-*dimethyl*-2-α-*carboxyethyl*- (poor yield), m.p. 91·5—92·5°, -2-α-*carboxy*isopropyl-, m.p. 89—89·5°, and -2-β-*carboxyethyl*-, m.p. 56—57°, -4 : 5-*benz*-1 : 3-*dioxole*. (**II**) and (**III**) are stable in aq. alkali. An electronic mechanism for the cleavage is postulated, involving $^-O{\cdot}C_6H_4{\cdot}O{\cdot}CMe{:}CH{\cdot}CO_2Et$, supported by the relative ease of hydrolysis, ketone > esters > acids. R. S. C.

Oxygen absorption induced by ether linkings. Rates of oxygen absorption by dioxolan and methyldioxolan. R. R. Legault and D. C. Lewis (*J. Amer. Chem. Soc.*, 1942, **64**, 1354—1356).—Pure dioxolan (**I**), b.p. 75·0—75·2° (corr.), and methyldioxolan (**II**), b.p. 85·3—85·5° (corr.), absorb O_2 in light (not in the dark), (**I**) immediately, (**II**) after an induction period, but the rate of absorption soon decreases. Bz_2O_2 (0·1 mol.-%) or natural peroxides (removed by distillation) accelerate the rate. The effect of inhibitors (2 mol.-%) is quinol > EtOH or H_2O. Absorption of O_2 is probably due to catalysis by peroxides formed *in situ*; the subsequent decrease in the rate may be due to inhibition by H_2O and EtOH formed by decomp. of these peroxides. R. S. C.

Dioxan derivatives.—See B., 1942, II, 315.

Cyclic ketals (dioxolans).—See B., 1942, II, 362.

Mixed anhydride of salicylic and carbonic acids; 5 : 6-benzo-1 : 3-dioxan-2 : 4-dione. A. Tschitschibabin (*Compt. rend.*, 1941, **213**, 355—357).—*o*-ONa·C_6H_4·CO_2Na and $COCl_2$ in PhMe at low temp. yield 5 : 6-*benzodehydro*-1 : 3-*dioxan*-2 : 4-*dione* (**I**), *o*-C_6H_4<CO·O / O—CO′>, decomp. 114° (cf. Dupont, B., 1935, 539), which has *M* (f.p. in C_6H_6) 166, but does not analyse satisfactorily. (**I**) is decomposed by H_2O to CO_2 and *o*-OH·C_6H_4·CO_2H. With MeOH, (**I**) yields only *o*-CO_2H·C_6H_4·O·CO_2Me, decomp. 138° (block), thus confirming the above structure. (**I**) and EtOH yield *o*-CO_2H·C_6H_4·O·CO_2Et, m.p. 95°. C. S.

Synthesis of diphenylene dioxide derivatives. VIII. Synthesis of dihydroxydiphenylene dioxide phosphoric ester. M. Tomita (*J. Pharm. Soc. Japan*, 1936, **56**, 490—492).—2 : 6-*Dihydroxydiphenylene dioxide*, m.p. 269° (*diphosphoric ester*, m.p. 236°), was obtained by heating the $(OMe)_2$-compound with HBr–AcOH. 1 : 5-*Dihydroxy*-3 : 7-*dimethyldiphenylene dioxide diphosphoric ester* has m.p. 198°. Ch. Abs. (*c*)

Indigoid dyes.—See B., 1942, II, 318.

Ammonium character of pyrrole and its derivatives. E. Weitz and F. Schmidt (*J. pr. Chem.*, 1941, [ii], **158**, 211—232).—Reactions of pyrrole and its derivatives are best understood by regarding them as N^{IV} radicals. *E.g.*, they form unstable, coloured quin-

hydrones with quinones and the following are isolated from $COMe_2$, light petroleum, C_6H_6, or Et_2O at low temp. (*a*) 1 : 1 *Compounds* of 1 : 2 : 5-trimethylpyrrole (**I**) with chloranil (**II**), 2 : 6- (**III**) or 2 : 3-dichloro-*p*-benzoquinone (**IV**), and a (?) 2 : 3 *compound* with 2 : 5-dibromo-*p*-benzoquinone; (*b*) 1 : 1 *compounds* of 2 : 5-dimethylpyrrole with (**II**) or (**III**), and a (?) 3 : 2 *compound* with (**IV**); (*c*) a 1 : 1 *compound* of 2 : 4-dimethylpyrrole and (**IV**); (*d*) 1 : 1 *compounds* of naphthadiquinone with indole, decomp. ~110—115°, or *N*-methylcarbazole (**V**), and a 1 : 2 *compound* with carbazole, decomp. from 150—155°; (*e*) 1 : 1 *compounds* from quinazarinquinone with carbazole, (**V**), or *N*-ethylcarbazole, and a 1 : 2 *compound* with indole. 2-Acetylpyrrole gives a 1 : 1 *compound* with $AgClO_4$ in Et_2O. SO_2 gives 1 : 1 *compounds* with (**I**) or *N*-phenylcarbazole. The components are readily regenerated in many cases. With many other combinations coloured solutions, but no solids, are obtained. R. S. C.

Quantitative investigations of amino-acids and peptides. IX. Physical properties of *l*(−)-histidine. M. S. Dunn, E. H. Frieden, M. P. Stoddard, and H. V. Brown (*J. Biol. Chem.*, 1942, **144**, 487—500; cf. A., 1942, II, 165).—*l*(−)-Histidine (**I**), $[\alpha]_D^{25}$ −38·95°±0·06° in H_2O, $[\alpha]_D^{24·8}$ +13·34°±0·02° in 6·08N-HCl, of 99·5% purity, may be prepared by fractional crystallisation from H_2O and EtOH of material isolated from protein hydrolysates. The solubility of (**I**) is 4·286±0·013 g. per 100 g. of H_2O. The val. of $[\alpha]$ in H_2O, aq. EtOH, or 6N-HCl varies little with concn. of solute, but variations are noticed in 0·01—0·1N-HCl. In solvents other than H_2O $[\alpha]$ is dependent on the dipole moment, but not on the dielectric const., of the solvent. Temp. coeffs. of $[\alpha]_D$ of (**I**) and other NH_2-acids are compared. A. T. P.

Friedel–Crafts acylation of indoles and quinolines. W. Borsche and H. Groth (*Annalen*, 1941, **549**, 238—255).—Indoles are " acetylated " by AcCl or Ac_2O at 100° at $C_{(2)}$ or $C_{(3)}$ or, if these positions are occupied, by (usually) AcCl–$AlCl_3$ in CS_2 in the *Bz*-nucleus, the reaction being facilitated by 4- and 6-alkyl. Quinoline, *iso*quinoline, acridine, 6- and 8-methyl- and 6 : 8-dimethyl-quinoline cannot, but other quinoline derivatives can, be acylated. Ac_2O and 2-methyl- gives 3-acetyl-2-methyl-indole (40%), cryst. (2 : 4-dinitrophenylhydrazone, m.p. 263—264°), but boiling AcCl gives α-2-*methyl*-3-*indolyl*-α-2′-*methyl*-3′-*indolidene*-*ethane hydrochloride*, decomp. 160°, and thence the *ψ-base anhydride*, m.p. 208°. 2-Phenylindole gives similarly 3-*acetyl*-, m.p. 220—221° (2 : 4-*dinitrophenylhydrazone*, m.p. 282—283°), + *xy*-*diacetyl*-2-*phenylindole*, m.p. 275—277°, and α-2-*phenyl*-3-*indolyl*-α-2′-*phenyl*-3′-*ψ*-*indolidene*-*ethane*, m.p. 247° (hydrochloride). 1 : 2-Dimethylindole with boiling Ac_2O gives 3-, m.p. 103—104° [2 : 4-*dinitrophenylhydrazone*, m.p. 259° (decomp.)], and with AlCl–$AlCl_3$ gives 5-*acetyl*-1 : 2-*dimethylindole*, m.p. 157° (2 : 4-*dinitrophenylhydrazone*, m.p. 263—264°). 1 : 2 : 3-*Trimethyl*-5-*indolyl Me ketone*, m.p. 123°, b.p. 306—308° (2 : 4-dinitrophenylhydrazone, m.p. 258°), is obtained from the Me_3 compound by AcCl–$AlCl_3$ in boiling CS_2. 2 : 3-Dimethylindole with boiling AcCl gives 2 : 3-*dimethyl*-5-*indolyl Me ketone* (85%), m.p. 74°, and with $AlCl_3$–AcCl in boiling CS_2 gives 1 : 6-*diacetyl*-2 : 3-*dimethylindole*, m.p. 115—116°, b.p. 220—225°/3 mm., and thence (N-KOH–MeOH) 2 : 3-*dimethyl*-6-*indolyl Me ketone* m.p. 153° (*oxime*, m.p. 217°; 2 : 4-*dinitrophenylhydrazone*, m.p. 278—279°). s-m-*Xylylhydrazine* [prep. from *s*-*m*-xylidine (**I**) by $NaNO_2$–HCl and then $SnCl_2$–HCl], m.p. 82° (*Bz* derivative, m.p. 164°), and COMeEt give the hydrazone, b.p. 160—162°/13 mm., converted by $ZnCl_2$ at 170° into 2 : 3 : 4 : 6-*tetramethylindole*, m.p. 128—129°, b.p. 179—180°/13 mm., which with boiling AcCl gives 2 : 3 : 4 : 6-*tetramethyl*-1-, m.p. 101°, and with AcCl–$AlCl_3$ in warm CS_2 gives the -5-*indolyl Me ketone*, m.p. 152° (2 : 4-*dinitrophenylhydrazone*, m.p. 256—257°). 2 : 4 : 1-$C_6H_3Me_2$·NH·N:CMeEt, b.p. 157—158°/16 mm., and $ZnCl_2$ at ~70° (later 120°) give 2 : 3 : 5 : 7-*tetramethylindole*, m.p. 95—96°, b.p. 164—165°/16 mm. (*picrate*, m.p. 161—162°). This or its 1-Ac derivative with AcCl–$AlCl_3$–CS_2 give only a trace of ketone (2 : 4-dinitrophenylhydrazone, m.p. 284—285°). *o*-OMe·C_6H_4·NH·N:CMeEt, b.p. 170°/18 mm., with $ZnCl_2$ or, better, HCl in aq. AcOH at 100° gives 7-*methoxy*-2 : 3-*dimethylindole*, b.p. 166°/14 mm. (*picrate*, m.p. 171—172°), which is unaffected by boiling AcCl but with AcCl–$AlCl_3$ in boiling CS_2 gives 7-*methoxy*-2 : 3-*dimethyl*-4-*indolyl Me ketone*, m.p. 159° (*picrate*, m.p. 192—193°; 2 : 4-*dinitrophenylhydrazone*, m.p. 258—259°) (and a *substance*, m.p. 191°), and with BzCl–$AlCl_3$–CS_2 gives the 4-*Bz* derivative, m.p. 183—184° (2 : 4-*dinitrophenylhydrazone*, m.p. 206—207°). 5 : 7-Dimethylquinoline [prep. from (**I**) by glycerol, $PhNO_2$, and conc. HCl], b.p. 273—275° (*hydrochloride*, m.p. 243—244°; *picrate*, m.p. 240—241°; *methiodide*, m.p. 206°), with AcCl–$AlCl_3$–CS_2 at the b.p. and later room temp. gives 5 : 7-*dimethyl*-6-*quinolyl Me ketone*, m.p. 74—76° (2 : 4-*dinitrophenylhydrazone*, m.p. 283—285°). 8-Methoxyquinoline with AcCl– or BzCl–$AlCl_3$–CS_2 gives 8-*methoxy*-5-*quinolyl Me* (**II**), m.p. 125—126°, b.p. 210—212°/30 mm. (*picrate*, m.p. 175°; *oxime*, m.p. 208—209°; 2 : 4-*dinitrophenylhydrazone*, m.p. 218—220°), and *Ph ketone*, m.p. 115°, respectively; with CH_2Cl·COCl–$AlCl_3$–CS_2 it gives 8-hydroxy-5-chloroacetylquinoline. 8-Acetoxyquinoline, m.p. 56—57° (lit., b.p. ~280°), with $AlCl_3$ in $PhNO_3$ gives 8-hydroxyquinoline. (**II**) could not be obtained from 8-hydroxy-5-acetylquinoline (CH_2N_2 gives a substance, m.p. 200°). Addition of CHMeAc·CO_2Et in $COMe_2$ to *p*-COMe·C_6H_4·N_2Cl–NaOAc–HCl–H_2O and keeping at room temp. and later 0° gives *Et γ-keto-β-p-acetylbenzeneazo-n-butyrate*, m.p. 146—148° (2 : 4-*dinitrophenylhydrazone*, m.p. 255°), which with $ZnCl_2$ at 140° gives *Et pyruvate*-p-*acetylphenylhydrazone*, m.p. 186° (decomp.), as sole isolable product. p-*Aminoacetophenone*-2 : 4-*dinitrophenylhydrazone* melts at 263°. 5-Cyano*iso*quinoline and MgMeI in boiling Et_2O give a little 5-acetyl*iso*quinoline (*semicarbazone*, m.p. 242°). R. S. C.

Syntheses in the quinoline series. IV. 2 : 4-Disubstituted quinoline derivatives. F. J. Buchmann and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1942, **64**, 1357—1360; cf. A., 1942, II, 150).—Prep. of 2 : 4-dihydroxy- and thence ($POCl_3$; 90°) of 2 : 4-dichloro-quinoline (**I**) (93%), m.p. 66—67°, is modified. With KOH–EtOH, (**I**) gives 4-chloro-2-ethoxy- (**II**) (31%) and 2-*chloro*-4-*ethoxy*-*quinoline* (**III**) (31%), m.p. 84°, and 4-chlorocarbostyril (**IV**) (5·5%) (cf. Friedlaender *et al.*, A., 1883, 351). The structure of (**III**) is proved by conversion [less ready than that of (**II**)] by boiling 6N-HCl into (**IV**) and by prep. (diazo-reaction in conc. HCl) from 4-amino-2-ethoxyquinoline (**V**). The 2-Cl of (**III**) is more reactive than the 4-Cl of (**II**), but both Cl of (**I**), (**II**), and (**III**) condense with bases at 140° or the b.p. Thus are obtained 2 : 4-*dimorpholino*-, m.p. 167—169°, 2 : 4-*di*-8′-*quinolylamino*-, m.p. 208—210°, 2-*morpholino*-4-*ethoxy*-, m.p. 146—147°, 2-*piperidino*-4-*ethoxy*-, m.p. 115°, and 4-*morpholino*-2-*ethoxy*-, sublimes at 110°, m.p. 140—150°, -*quinoline*, but NEt_2·$[CH_2]_3$·NH_2 gives gums. 2 : 4-*Diethoxyquinoline*, m.p. 56°, is obtained from (**I**), (**II**), or (**III**) by NaOEt. 70% HI converts (**III**) into 2-*chloro*-4-*hydroxyquinoline* (40%), m.p. 189—190°, which gives 2-*morpholino*-, m.p. 289—290° (decomp.), and 2-γ-*diethylamino*-n-*propylamino*-, m.p. 254—256° (decomp.), -4-*hydroxyquinoline*. With boiling Ac_2O, (**V**) gives 4-*acetamido*-2-*ethoxyquinoline*, m.p. 176—178°, and with boiling 70% HI gives 4-*aminocarbostyril* (70%), m.p. 308—310°. R. S. C.

Synthesis and characterisation of mono- and di-methylquinolines. R. H. F. Manske, L. Marion, and F. Leger (*Canad. J. Res.*, 1942, **20**, **B**, 133—152).—All the mono- and di-methylquinolines have been synthesised by unambiguous methods. The m.p. given in the literature for their derivatives are unreliable; the vals. now obtained [with m.p. in parentheses (italicised when new compounds) of the picrate, styphnate, and salt with trinitro-*m*-cresol] are: 2- (195°, 219°, 223°), 3- (**I**) (190°, 190°, 223°), 4- (220°, 237°, 254°), 5- (**II**) (223°, 218°, 214°), 6- (235°, 234°, 238°), 7- (242°, 242°, 243°), 8-methylquinoline (205°, 202°, 199°), 2 : 3-, m.p. 70° (235°, 243°, 248°), 2 : 4- (196°, 212°, 211°), 2 : 5- (**III**) (*223°, 207°, 201°*), 2 : 6-, m.p. 60° (191°, 200°, 206°), 2 : 7-, m.p. 61° (*196°*, 222°, 250°), 2 : 8- (183°, 194°, 209°), 3 : 4- (**IV**), m.p. 74° (221°, 232°, 237°), 3 : 5- (**V**) (*220°, 214°, 221°*), 3 : 6-, m.p. 58° (*253°, 234°, 255°*), 3 : 7-, m.p. 80° (*244°, 214°, 222°*; *perchlorate*, m.p. 216°), 3 : 8- (210°, 205°, 208°), 4 : 5- (**VI**), m.p. 78° (*233°, 227°, 230°*), 4 : 6- (249°, 221°, 244°), 4 : 7- [230°, 272° (decomp.), 228°], 4 : 8-, m.p. 58° (229°, 231°, 231°), 5 : 6- (**VII**), m.p. 50° (*201°, 205°, 202°*), 5 : 7-, m.p. 22° (*249°, 247°, 239°*), 5 : 8-, m.p. 2° (186°, 184°, 180°), 6 : 7-, m.p. 58° [*278°*, 259° (decomp.), 262° (decomp.)], 6 : 8- (230°, 190°, 184°), 7 : 8-dimethylquinoline (*198°, 179°, 214°*). The Cohn H_3BO_3 method using picric acid or *o*-NO_2·C_6H_4·OH as oxidant was used in the Skraup reactions. *p*-C_6H_4Br·NH_2 with CH_2:CMe·CHO yields 6-*bromo*-3-*methylquinoline*, m.p. 103° (*picrate*, m.p. 235°), debrominated (Zn–Cu, aq. NaOH, EtOH) to (**I**). 8-*Nitro*-5-*methylquinoline*, m.p. 138°, is reduced (Fe, HCl) to the 8-NH_2-compound, b.p. 115°/1·5 mm. (*hydrochloride*, decomp. 200°; *picrate*, m.p. 234°), which (HNO_2, H_3PO_2) gives (**II**). 8-*Nitro*-2 : 5-*dimethylquinoline*, m.p. 174°, is reduced (Fe, HCl–EtOH) to the 8-NH_2-compound, b.p. 110—115°/1·5 mm. (*picrate*, m.p. 189°), which (HNO_2, H_3PO_2) gives (**III**). (**IV**), CCl_3·$CH(OH)_2$, and $ZnCl_2$ on a steam bath give *γγγ-trichloro*-α-(3-*methyl*-4-*quinolyl*)-*propene*, m.p. 218°. 4-Nitro-*m*-toluidine (**VIII**) and CH_2:CMe·CHO (HCl, $ZnCl_2$) afford 8-*nitro*-3 : 5-*dimethylquinoline*, m.p. 192°, reduced (Fe, HCl–EtOH) to the 8-NH_2-compound (*picrate*, m.p. 214°), which (HNO_2, H_3PO_2) gives (**V**). (**VIII**) + COMe·CH_2·CH_2·OH yields 8-*nitro*-4 : 5-*dimethylquinoline*, m.p. 140°, reduced (Fe, HCl) to the 8-NH_2-compound, m.p. 97°, which gives (**VI**) (HNO_2, H_3PO_2). 8-*Nitro*-5 : 6-*dimethylquinoline*, m.p. 166°, is reduced ($SnCl_2$, HCl) to the 8-NH_2-compound, m.p. 78—79° (*picrate*, m.p. 213°), which with HNO_2–EtOH gives (**VII**) and 8-*ethoxy*-5 : 6-*dimethylquinoline* (*picrate*, m.p. 224°). 7-Ethylquinoline (picrate, m.p. 229°; styphnate, m.p. 268°; salt with trinitro-*m*-cresol, m.p. 240°) was obtained in 91·8% yield. 5-Methylisatin with COMeEt yields 2 : 3 : 6-*trimethylquinoline*-4-*carboxylic acid*, which on distillation gives 2 : 3 : 6-trimethylquinoline, m.p. 87·5° (picrate, m.p. 217°; styphnate, m.p. 238°; salt with trinitro-*m*-cresol, m.p. 224°). 7-Methylisatin similarly gives 2 : 3 : 8-trimethylquinoline, m.p. 56—57° (picrate, m.p. 252°; styphnate, m.p. 239°; salt with trinitro-*m*-cresol, m.p. 227°). *m*-C_6H_4Me·NH_2 and CHAcMe·CH_2·OH yield 3 : 4 : 7-trimethylquinoline, m.p. 78° (picrate, m.p. 229°; styphnate, m.p. 234°; salt with trinitro-*m*-cresol, m.p. 218°). All m.p. are corr. W. C. J. R.

Derivatives of 4-amino-6-methoxyquinaldine. W. F. Holcomb and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1942, **64**, 1309—1311).—NH_2·$[CH_2]_3$·NH_2, substituted in one NH_2 (4 examples), are readily

prepared from the substituted β-aminopropionitriles by H_2–Raney Ni (*e.g.*, in EtOH at 70°/4 atm.). *β-Di-n-amylaminopropionitrile* (prep. from CH_2:CH·CN and NHR_2 at 50° and later room temp.), b.p. 136°/6 mm., and *NN*-di-*n*-amylpropylenediamine, b.p. 129°/6 mm. (*dipicrate*, m.p. 192—193°), are described. 4-Chloro-6-methoxy-2-methylquinoline with the appropriate amine at the temp. given in parentheses gives 4-2′-*pyridylamino*- (in boiling Cellosolve), m.p. 199—200°, 4-8′-*quinolylamino*- (160—175°), m.p. 184—186°, 4-6′-*methoxy*-8′-*quinolylamino*- (160—175°), m.p. 200—201°, 4-5′-*indazolylamino*- (160—175°), m.p. 303—305°, 4-γ-diethylamino-α-propylamino- (175°) (*dihydrochloride*, +$2H_2O$, m.p. 126—127°), 4-γ-*morpholino*-n-*propylamino*- (175°), +$3H_2O$, m.p. 165—166°, 4-δ-diethylamino-α-methyl-*n*-butylamino- (225°) (*dihydrochloride*, +$2H_2O$, m.p. 222—223°), and 4-*morpholino*- (140°), m.p. 124—125°, -6-*methoxy*-2-*methylquinoline* and 3 : 7-*di*-6′-*methoxy*-2′-*methyl*-4′-*quinolylthionine* (160—175°), m.p. 208—210°. R. S. C.

Constitution of the autoxidation products of indandione anils. P. Pfeiffer and E. Jaensch (*J. pr. Chem.*, 1941, [ii], **159**, 241—263).—*iso*Quinoline derivatives have been synthesised to support Pfeiffer's formula for the autoxidation products of substituted indandione anils. *o*-$C_6H_4Bz{\cdot}CO_2Me$, KCN, and $(NH_4)_2CO_3$ (20 atm. CO_2, 100—110°, 6 hr.) afford (*a*) 3-*cyano*-3-*phenylphthalimidine* (**I**), m.p. 227° (*acetate*, m.p. 145°), and not 5-phenyl-5-*o*-carboxyphenylhydantoin, and (*b*) 3-*carbamyl*-3-*phenylphthalimidine* (**II**), m.p. 269—270°. With H_2O_2 (**I**) gives (**II**) and with HCl—EtOH affords 3-phenylphthalimidine (**III**), m.p. 218—220°, re-melts 295—298° (acetate, m.p. 154—155°). (**II**) with H_2SO_4 and $NaNO_2$ gives 3-*phenylphthalimidine*-3-*carboxylate* [warming gives CO_2 and (**III**)], which with CH_2N_2 gives the *Me* ester, m.p. 165° [with NH_3 affords (**II**)]. *o*-$C_6H_4(CO)_2O$ and $CH_2Ph{\cdot}CO_2H$ yield 3-benzylidenephthalide, converted into *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Ph$, and then into benzil-*o*-carboxylic acid (**IV**), With KOH (**IV**) affords 3-*carboxy*-3-*phenylphthalide hydrate* (**V**) (not *o*-carboxydiphenylglycollic acid), which when heated gives *phenylphthalide* (**VII**), m.p. 115°. (**V**) is dehydrated to the *acid lactone*, m.p. 128—130°, and gives (Me_2SO_4 or CH_2N_2) the *Me* ester (**VI**), m.p. 96°; (**VI**) with NH_3 affords 3-*phenylphthalide*-3-*carboxylamide* (**VIII**), m.p. 224° [with KOH affords (**V**)], and with H_2SO_4–$NaNO_2$ gives a *compound*, m.p. 78—85°, which when heated (100°) gives (**VII**) and treated with CH_2N_2 gives (**VI**). (**VIII**) with NH_3 affords 4-*hydroxy*-1 : 3-*diketo*-4-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (**IX**), m.p. 193° (with H_2SO_4 gives a halochromic *substance*, m.p. 230—235°), converted by KOH into (**V**). (**VI**) with NH_2Me yields 3-*phenylphthalide*-3-*carboxymethylamide*, m.p. 168°, and 4-*hydroxy*-1 : 3-*diketo*-4-*phenyl*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (**XI**), m.p. 107°. (**VIII**) with NH_2Ph gives 3-*phenylphthalide*-3-*carboxylanilide*, m.p. 131°, and with *p*-anisidine yields 3-*phenylphthalide*-3-*carboxy*-p-*anisidide*, m.p. 172°. (**IX**) with *p*-anisidine affords 3-*phenyl*-2-p-*anisylphthalimidine*, m.p. 201°. (**IX**) with *p*-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$ yields 3-*phenyl*-2-p-*dimethylaminophenylphthalimidine*, m.p. 270—271°. $OH{\cdot}CPh_2{\cdot}CO_2Me$ and PhNCO yield 2 : 4-diketo-3 : 5 : 5-triphenyloxazolidine, m.p. 143°, converted into $OH{\cdot}CPh_2{\cdot}CO{\cdot}NHPh$, m.p. 176°. C. S.

Glyoxalines. I. Hydantoins resulting from the reaction between phenylglyoxal and carbamide and substituted carbamides. H. J. Fisher, J. B. Ekeley, and A. R. Ronzio (*J. Amer. Chem. Soc.*, 1942, **64**, 1434—1436).—$PhCO{\cdot}CHO,H_2O$ (**I**) and $CO(NH_2)_2$ (**II**) in aq. KOH at < the b.p. (3 min.) give 4-phenylhydantoin (**III**) (85%) (*Ac* derivative, m.p. 145°), but when boiled for 1 hr. in more dil. KOH give 2-*keto*-4 : 5-*dihydroxy*-4-*phenyltetrahydroglyoxaline* (**IV**), which at the m.p. (184°) or in HCl–EtOH loses H_2O to give (**III**) but with AcCl– or Ac_2O–C_5H_5N gives tars. In boiling AcOH or 6N-HCl, (**I**) + (**II**), (**III**), or (**IV**) give a *polymeride*, m.p. >340°, of (**III**). In boiling dil. KOH, (**I**) and $NHPh{\cdot}CO{\cdot}NH_2$ or $NHMe{\cdot}CO{\cdot}NH_2$ give 2-*keto*-4 : 5-*dihydroxy*-3 : 4-*diphenyltetrahydroglyoxaline*, m.p. 169—170° (gas) (and thence, as above, 3 : 4-*diphenylhydantoin*, m.p. 189—190°), and 4-*phenyl*-3-*methylhydantoin*, m.p. 174°, respectively. Absorption spectra are given. R. S. C.

Oxidation of pyrazolines obtained from unsymmetrical dibenzylideneacetones. R. H. Manley and L. C. Raiford (*Proc. Iowa Acad. Sci.*, 1935, **42**, 121).—The derivatives of unsymmetrical dibenzylideneacetones containing vanillylidene residues were oxidised to substituted pyrazoles and BzOH by $KMnO_4$ in C_5H_5N.

CH. ABS. (*c*)

Stereoisomeric derivatives of antipyrinaldehyde [5-keto-1-phenyl-2 : 3-dimethylpyrazole-4-aldehyde]. M. Ridi (*Gazzetta*, 1941, **71**, 95—100).—2-Iodo-5-keto-1-phenyl-2 : 3-dimethyl-4-*p*-phenetyliminomethylpyrazole (**I**), or the corresponding 4-anilomethyl compound, heated with aq. KOH, followed by AcOH and NH_2OH,HCl, gives an *oxime* (**II**), m.p. 228—230°, of 5-keto-1-phenyl-2 : 3-dimethylpyrazole-4-aldehyde (**III**), isomeric with that of m.p. 220—221° (Passerini *et al.*, A., 1940, II, 56). By similar means a *phenylhydrazone*, m.p. 253—255°, isomeric with that of m.p. 190—192° (*loc. cit.*), and a p-*nitrophenylhydrazone*, m.p. 276—280°, isomeric with that of m.p. 240—242° obtained directly from (**III**), and a *semicarbazone*, m.p. 249—251°, isomeric with that of m.p. 204—208° (*loc. cit.*) are obtained. In boiling Ac_2O, (**II**) gives 4-cyano-1-phenyl-2 : 3-dimethyl-5-*iso*pyrazolone (A., 1940, II, 55). It is suggested that the isomerides obtained directly have the *anti*, and those obtained as above the *syn*, configuration. E. W. W.

Reaction between methyl iodide and Schiff's bases at 120—130°. M. Ridi (*Gazzetta*, 1941, **71**, 100—105).—5-Keto-1-phenyl-3-methyl-4-*p*-phenetyliminomethylpyrazole-4-aldehyde with MeI, with or without EtOH, at 120—130° gives its 2-*methiodide*, m.p. 210—212°, which with further MeI and MeOH at 120—130° gives *p*-$OEt{\cdot}C_6H_4{\cdot}NMe_3I$ (**I**) and a product which with boiling aq. KOH followed by AcOH–$NHPh{\cdot}NH_2$ gives the *phenylhydrazone*, m.p. 253—255°, of 5-keto-1-phenyl-2 : 3-dimethylpyrazole-4-aldehyde (see preceding abstract). 5-Keto-1-phenyl-3-methyl-4-anilomethylpyrazole-4-aldehyde and MeI–MeOH at 120—130° give a product, m.p. 190—191°. *p*-$OEt{\cdot}C_6H_4{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OMe$-*p* with MeI–MeOH at 120—130° gives (**I**). E. W. W.

Pyrazolone derivatives. M. Ridi (*Gazzetta*, 1941, **71**, 106—111).—The oxime (**I**), m.p. 254°, of 5-keto-1 : 3-diphenyl-2-methylpyrazole-4-aldehyde (**II**) with boiling Ac_2O gives 4-*cyano*-1 : 3-*diphenyl*-2-*methyl*-5-iso*pyrazolone*, m.p. 188° (also obtained from 4-cyano-1 : 3-diphenyl-5-pyrazolone and MeI at 130—135°); the facile formation of the reaction suggests that (**I**) has the *syn* form. *p*-Phenetylformamidine and 1 : 3-diphenyl-5-pyrazolone in boiling EtOH give 1 : 3-*diphenyl*-4-p-*phenetyliminomethyl*-5-*pyrazolone*, m.p. 124—125°, which with MeI—MeOH at 120—130°, followed by $NHPh{\cdot}NH_2$, gives the *phenylhydrazone* (**III**), m.p. 260—262°, of (**II**). The anil of (**II**), after heating with aq. KOH, with AcOH and $NHPh{\cdot}NH_2$ gives (**III**); it similarly gives (**I**), and the *semicarbazone*, m.p. 256—258°, p-*nitrophenylhydrazone*, m.p. 290°, and *aminoguanidine* derivative, m.p. 274—276° (decomp.), of (**II**). 2-Iodo-5-keto-1-phenyl-2 : 3-dimethyl-4-*p*-phenetyliminomethylpyrazole with aq. KOH followed by aminoguanidine and AcOH gives the *aminoguanidine* derivative, m.p. 244—248° (decomp.), of 5-keto-1-phenyl-2 : 3-dimethylpyrazole-4-aldehyde, isomeric with the derivative previously described (*Gazzetta*, 1940, **70**, 413). E. W. W.

Structure of *o*-dinitrosobenzenes. II. G. Tappi (*Gazzetta*, 1941, **71**, 111—117).—The dipole moments of (*a*) benzfurazan and its 3- and 5-Me, 3 : 5-Me_2, 5-Cl-, and 3-NO_2-derivatives, and (*b*) of "dinitrosobenzene" (benzfurazan 1-oxide) (cf. A., 1940, II, 58) and its 6- and 4-Me, 4 : 6-Me_2, 4-Cl-, 6- and 4-NO_2-, and 4 : 6- and 4 : 5-$(NO_2)_2$-derivatives, are determined in dioxan. They agree with those calc. on a plane benzfurazan 1-oxide structure for group (*b*); the NO_2 group in the 4-position appears to be partly tautomerised into the *aci*-form. E. W. W.

Pyrogenic oxido-reduction of benzylidene-*o*-phenylenediamine. G. B. Crippa and S. Maffei (*Gazzetta*, 1941, **71**, 194—200).—*o*-$NH_2{\cdot}C_6H_4{\cdot}N{:}CHPh$ at 230° in CO_2 gives *o*-$C_6H_4(NH_2)_2$ (**I**), 2-phenylbenziminazole (**II**), *o*-$NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2Ph$ (**III**), and 2-phenyl-1-benzylbenziminazole (**IV**). At 65° in H_2 the products are (**I**), (**II**), (**III**), and *o*-$C_6H_4(N{:}CHPh)_2$ (**V**), which at its m.p. (106°) gives (**IV**). The formation of (**II**) and (**III**), and of (**I**) and (**V**) or (**IV**), is ascribed to two parallel oxidation–reduction processes. The intermediate formation of *o*-$NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}CHPh{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}CHPh$-*o* is suggested. E. W. W.

Condensation of pyrroles with propiolic and pyruvic acid. H. Fischer and H. Gademann (*Annalen*, 1942, **550**, 196—207).—Et 2 : 4-dimethylpyrrole-5-carboxylate (**I**) with $CH{\equiv}C{\cdot}CO_2H$ (**II**) in AcOH at 110° gives *αβ-di-5-carbethoxy*-2 : 4-*dimethyl*-3-*pyrrylethane* (**III**), m.p. 249°, which is formed by way of β-5-carbethoxy-2 : 4-dimethyl-3-pyrrylacrylic acid and Et 2 : 4-dimethyl-3-vinylpyrrole-5-carboxylate since these intermediates separately give (**III**) when boiled with (**I**) in AcOH. Most analogues of (**I**) react too vigorously or not at all with (**II**), but Et 2-methylpyrrole-5-carboxylate (**IV**) gives, after long boiling, *αβ-di-5-carbethoxy*-2-*methyl*-3-*pyrrylethane*, m.p. 186°. $[CH(OMe)_2]_2$ and (**I**) with a trace of H_2SO_4 in boiling EtOH give *aaββ-tetra-5-carbethoxy*-2 : 4-*dimethyl*-3-*pyrrylethane*, m.p. 220°. Et 3-formyl-2 : 4-dimethylpyrrole-5-carboxylate (1 mol.) with (**I**) (2 mols.) in Ac_2O at 120° gives *tri-5-carbethoxy*-2 : 4-*dimethyl*-3-*pyrrylmethane*, m.p. 182°. An excess of MeCHO with (**I**) and 2 drops of HCl in boiling EtOH yields *aa-di-5-carbethoxy*-2 : 4-*dimethyl*-3-*pyrrylethane*, m.p. 244°. $AcCO_2H$ and (**I**) at the b.p. give, by formation of $OH{\cdot}CMeR{\cdot}CO_2H$ and then dehydration, *α-5-carbethoxy*-2 : 4-*dimethyl*-3-*pyrrylacrylic acid* (**V**) (~100%), m.p. 228° (decomp.) (*Me* ester, m.p. 116°), hydrogenated (Pd; AcOH; best 60—80°) to *α-5-carbethoxy*-2 : 4-*dimethyl*-3-*pyrrylpropionic acid*, m.p. 183°. 5-Acetyl-2 : 4-dimethylpyrrole and $AcCO_2H$ at 100° give similarly *α-5-acetyl*-2 : 4-*dimethyl*-3-*pyrrylacrylic acid*, m.p. 213°, but (**IV**) and $AcCO_2H$ give *aa-di-5-carbethoxy*-2-*methyl*-3-*pyrrylpropionic acid*, m.p. 246°, and Et 2 : 4-dimethylpyrrole-3-carboxylate gives similarly *aa-di-4-carbethoxy*-3 : 5-*dimethyl*-2-*pyrrylpropionic acid*, m.p. 163°. Attempts to decarboxylate or remove CO_2Et from (**V**) failed, but boiling HI–AcOH gives α-2 : 4-*dimethyl*-3-*pyrrylpropionic acid*, m.p. 93°. R. S. C.

Pyrrole series. VIII. Structural investigations of a substituted dipyrrylmethane. An unusual m.p.–symmetry relationship. A. H. Corwin, W. A. Bailey, jun., and P. Viohl (*J. Amer. Chem. Soc.*, 1942, **64**, 1267—1273; cf. A., 1942, II, 330).—Reactions below

prove that the reaction, $2CH_2X{\cdot}OH \rightarrow CH_2X_2 + CH_2O + H_2O$ [X = a pyrryl group), does not involve N and indicate as the probable course: $CH_2X{\cdot}OH \rightleftharpoons XH + CH_2O$; $CH_2X{\cdot}OH + XH \rightarrow CH_2X_2 + H_2O$. *Et*$_2$ 4-*methyl*-2-*chloromethylpyrrole*-3 : 5-*dicarboxylate* (**I**) [prep. from the 2 : 4-Me_2 compound (**II**) by SO_2Cl_2–AcOH at 50—60°, later 70°; 71% yield], m.p. 156°, is hydrolysed by Na_2CO_3–$COMe_2$–H_2O to the 2-$CH_2{\cdot}OH$ compound (**III**) (~90%), m.p. 120—121° (decomp.), and converted by boiling AcOH, later aq. AcOH, into 3 : 5 : 3′ : 5′-tetracarbethoxy-4 : 4′-dimethyldipyrrylmethane (**IV**) (57%), which is also obtained from (**III**) and $KHSO_4$ at 130—135° (93% yield) or in boiling xylene (~100%). Addition of Na to (**IV**) in PhMe at 105—110° and then of Me_2SO_4 at 90° and finally boiling gives 3 : 5 : 3′ : 5′-*tetracarbethoxy*-1 : 4 : 4′-*tri*- (90—95%), m.p. 139—140°, and thence 1 : 4 : 1′ : 4′-*tetra-methyldipyrrylmethane* (**V**) (97%), m.p. 144—145°. Et$_2$ 1 : 2 : 4-trimethyl- [prep. from (**II**) improved] gives, as above, *Et*$_2$ 1 : 4-*dimethyl*-2-*chloromethyl*- (**VI**) (80%), m.p. 71—72°, and thence 2-*hydroxymethyl*-*pyrrole*-3 : 5-*dicarboxylate*, m.p. 98° [also obtained (70%) by methylation, as above, of (**III**)]. In H_2O–AcOH, (**VI**) gives 30% of (**V**). Et 2 : 4-dimethylpyrrole-3-carboxylate and (**I**) in boiling MeOH give 4 : 3′ : 5′-tricarbethoxy-3 : 5 : 4′-trimethyldipyrrylmethane, m.p. 157°, which, like two other compounds, cannot be methylated. Treatment of (**I**) or (**II**) in AcOH with 1 mol. or 2 mols., respectively, of SO_2Cl_2 at 50—60° gives Et$_2$ 2-formyl-4-methylpyrrole-3 : 5-dicarboxylate (**VII**), m.p. 124—125°. Treatment of (**II**) in AcOH with Br at 14° and then with SO_2Cl_2 at 14°, lowered to 0—2°, and finally raised to 60°, and addition of H_2O gives 70—75% of 3 : 5-*dicarbethoxy*-4-*methylpyrrole*-2-*carboxylic acid* (**VIII**), m.p. 150°, with 13—17% of (**VII**). Decarboxylation of (**VIII**) yields tars. Addition of Br to (**VIII**) in AcOH at 40—45° and then of H_2O at 45° and heating at 100° gives Et$_2$ 2-bromo-4-methylpyrrole-3 : 5-dicarboxylate (**IX**) (77%), m.p. 145°, hydrogenated (Pd–C, MeOH; 2 atm.) to *Et*$_2$ 3-*methylpyrrole*-2 : 4-*dicarboxylate* (**X**), m.p. 91°, the structure of which is confirmed by bromination to (**IX**). Two similar debrominations are also recorded. (**IV**) is also prepared from (*a*) (**X**), 36% aq. CH_2O, and conc. HCl in boiling AcOH, (*b*) Et$_2$ 4-methyl-2-hydroxymethylpyrrole-3 : 5-dicarboxylate (**XI**) in HCl–AcOH–H_2O, and (*c*) (**XI**) and (**X**) in HCl–AcOH–H_2O. Some of the products have unexpected m.p. R. S. C.

1 : 9-Pyrazolanthrone-6-carboxylic acid.—See B., 1942, II, 363.

Synthesis of glyoxaline derivatives from α-oximinoketones. Synthesis of 4-β-piperidylglyoxaline. E. Ochiai and S. Ikuma (*J. Pharm. Soc. Japan*, 1936, **56**, 525—531).—Reduction of OH·N:CAc·CO_2Et, CAcMe:N·OH, and Et oximinonicotinoacetate with Pd–C and treatment with KCNS or NH_4CNS gives respectively *Et* 2-*thiol*-4-*methylglyoxaline*-5-*carboxylate*, m.p. 229°, 2-*thiol*-4 : 5-*dimethylglyoxaline*, m.p. 270°, and *Et* 2-*thiol*-4-β-*pyridylglyoxaline*-5-*carboxylate* (**I**), m.p. 230—231°. The use of KCNO instead of KCNS affords *Et* 2-*hydroxy*-4-*methylglyoxaline*-5-*carboxylate*, m.p. 220°, 2-*hydroxy*-4 : 5-*dimethylglyoxaline*, m.p. 210°, and *Et* 2-*hydroxy*-4-*pyridylglyoxaline*-5-*carboxylate*, m.p. 258° (decomp.), respectively. (**I**) is oxidised by H_2O_2 to *Et* 4-*pyridylglyoxaline*-5-*carboxylate*, m.p. 198°, which is hydrolysed and decarboxylated to 4(5)-*pyridylglyoxaline* and thence reduced to 4(5)-β-*piperidylglyoxaline* (*hydrochloride*, m.p. 188—190°; *picrate*, m.p. 227°; *monobenzoate*, m.p. 192°; *platinichloride*). CH. ABS. (*c*)

1 : 3 : 5-Triazines.—See B., 1942, II, 316.

Nucleic acids. XX. Tetranucleotide of thymonucleic acid. H. Bredereck and I. Jochmann (*Ber.*, 1942, **75**, [*B*], 395—400).—Trituration with H_2O followed by treatment with EtOH–2N-HCl converts thymonucleic acid into the tetranucleotide (*Mg* salt, $[\alpha]_D^{20}$ +63·1° in H_2O), deaminated with formation of xanthine and hypoxanthine. H. W.

Nucleic acids. I. Degradation of thymonucleic acid by pancrease. F. G. Fischer, H. Lehmann-Echternacht, and I. Böttger (*J. pr. Chem.*, 1941, [ii], **158**, 79—94).—Isolation of nucleic acids is usually accompanied by degradation. The action of pancreas polynucleotidase (**I**) on thymonucleic acid (from calf's thymus) causes increase in conductivity, acidity, and power of depressing the f.p. (H_2O), decrease in η, and disappearance of precipitability by HCl. The mol. wt., determined by dialysis, lies between 1030 and 1730 (equiv. to 3·3—5·3 mononucleotide residues); the method, tested for ribonucleotides and riboguanylic acid, is inaccurate as the result depends on the concn. Titration of the extra acidity released by (**I**) indicates that the final product is a tetranucleotide. R. S. C.

Porphyrins. XLV. Synthesis of spirographis-porphyrin. H. Fischer and G. Wecker (*Z. physiol. Chem.*, 1941, **272**, 1—22).—The product of the action of MgMeI on the " 4-formyldeuteroporphyrin " of Fischer and Beer (A., 1937, II, 36) is a mixture (**I**) of 2- and 4-hydroxyethyldeuteroporphyrin ester (**II**) since reduction of the more freely sol. portion leads to 2-ethyldeuteroporphyrin ester, m.p. 214° (corr.). The isolation of homogeneous (**II**) from the mixture is tedious. Deuterohæmin ester is converted by $CHCl_2{\cdot}OEt$ (improved prep.) and $SnBr_4$ at 55° followed by conc. H_2SO_4 into formyldeuteroporphyrin Me_2 ester, m.p. 260° (additive products with cysteine and MeOH), which is hydrolysed and transformed by MgMeI into (**II**), m.p. 237° (corr.) (*Cu* salt, m.p. 218°). (**II**) is transformed by HBr–AcOH at room temp. followed by CH_2N_2 into 4-α-*methoxyethyldeuteroporphyrin Me*$_2$ *ester*, m.p. 192°. (**I**) is converted into two *acetates*, m.p. 233° (Kofler) and 210° (Kofler) respectively; the oxime of one of these is described. (**II**) is hydrolysed and the product is heated at 240°/high vac. and then converted by CH_2N_2 into 4-*vinyldeuteroporphyrin Me*$_2$ *ester*, m.p. 264° rapidly falling to 229° when kept; the corresponding *Fe* salt is converted by $CHCl_2{\cdot}OEt$ into spirographis-hæmin which when treated with Fe(OAc)$_2$–HCl or conc. H_2SO_4 gives spirographis-porphyrin (**III**) in spectroscopically recognisable amount. Formylation of 4-hydroxyethyldeuteroporphyrin ester Fe salt to 2-formyl-4-hydroxyethyldeuterohæmin and removal of H_2O from the free porphyrin with production of (**III**) proceeds smoothly but does not lead to cryst. products. 2-Formyl-4-hydroxyethyldeuteroporphyrin is heated at 240°/high vac. and the product is converted by CH_2N_2 into spirographis-porphyrin Me_2 ester, m.p. 281° (Kofler). The addition of HCN and $CHN_2{\cdot}CO_2Et$ to formyldeuteroporphyrin is described. Deuteroporphyrinacrylic acid is not decarboxylated to vinylporphyrin when heated at 330°/high vac.; when hydrogenated (Pd) it gives the propionic acid. Deuterohæmin (**IV**) is converted by Na and boiling *iso*-$C_5H_{11}{\cdot}OH$ followed by $FeCl_3$ into *deuterochlorin Me*$_2$ *ester*, m.p. 215°, and by $Cl{\cdot}[CH_2]_2{\cdot}OH$ and BF_3 in C_5H_5N into *deuteroporphyrin* ($Cl{\cdot}[CH_2]_2$)$_2$ *ester*, m.p. 190°. (**IV**), MeOH, and BF_3 yield deuteroporphyrin Me_2 ester and (**IV**), $CH_2Cl{\cdot}COCl$, and $AlCl_3$ followed by CH_2N_2 afford *deuterorhodin Me*$_2$ *ester*, m.p. 224°; this is converted by $(CH_2{\cdot}CO)_2O$ followed immediately by C_5H_5N or by warm C_5H_5N containing a little conc. HCl into deuteroverdin. H. W.

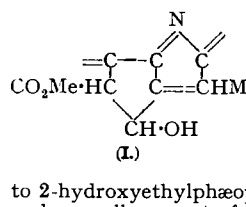
New bile pigments of the glaucobilin type from hæmins. E. Stier (*Z. physiol. Chem.*, 1942, **273**, 47—75).—Deuterohæmin in aq. C_5H_5N and N_2H_4,H_2O–aq. NaOH at 50° (O_2 is introduced for 5 min.; method: Warburg *et al.*, A., 1930, 1199), followed by treatment with HCl–MeOH and chromatographing, afford *deuteroglaucobilin Me*$_2$ *ester*, m.p. 284° or 288—289° (sinters at 205°). Tetramethylhæmatoporphyrin Fe salt similarly yields *tetramethylhæmatoglaucobilin*, $C_{27}H_{46}O_8N_4$, m.p. 220—222° (not sharp; sinters at 170°). Protohæmin and HBr–AcOH (shaken for 1·5 days), followed by NaOAc–Fe–AcOH (at 80°), yield the crude Fe salt of diacetylhæmatoporphyrin, and thence (MeOH–HCl) the corresponding crude Fe salt (**I**) of the Me_2 ester, and ($COMe_2$–AcOH–reduced Fe, in N_2) *diacetylhæmatoporphyrin Me*$_2$ *ester* (chromatographic purification) [Fe(OAc)$_2$–NaCl–AcOH gives the *Fe* complex]. (**I**) and aq. N_2H_4,H_2O–NaOH–O_2 at 55°, followed by MeOH–HCl, afford (probably) *diacetylhæmatoglaucobilin Me*$_2$ *ester*, m.p. 260° (sinters at 205°), converted by Na–MeOH–dioxan (in N_2) at 65—70°, followed by CH_2N_2, into *hæmatoglaucobilin Me*$_2$ *ester*, m.p. 225° (sinters at 180—195°). Pyrrohæmin and C_5H_5N–aq. N_2H_4,H_2O–NaOH–O_2 at 55°, then MeOH–HCl, yield *pyrroglaucobilin Me*$_2$ *ester*, $C_{31}H_{36}O_4N_4$, m.p. 305° (sinters at 227°), and phyllohæmin gives phylloglaucobilin Me_2 ester. A mixture of pigments is obtained by oxidising diacetylhæmato-Me_2 ester pyridineverdoparahæmatin in C_5H_5N with O_2 at 0°. A. T. P.

Chlorophylls. CXII. Racemisation of chlorophyll derivatives. H. Fischer and H. Gibian (*Annalen*, 1942, **550**, 208—251; cf. A., 1942, II, 274).—$C_{(7)}$ and $C_{(8)}$ of chlorophyll derivatives are both racemised by N_2H_4,H_2O–NaOMe–MeOH–C_5H_5N–N_2 at 115°. Structures are proved by absorption spectra, *X*-ray diagrams, and sometimes comparison with synthetic products. Figures in brackets below are λ of absorption bands (max. of broad bands in parentheses) in Et_2O in order of intensity. Purification involves chromatography. Mesodeoxopyrophæophorbide-*a* Me ester (**I**) {prep. [W. Lautenschlager] with, after oxidation, some deoxophylloerythrin (**II**), from pyrophæophorbide-*a* (**III**) by a little Pd–MeOH and H_2SO_4 in boiling HCO_2H}, m.p. 177° (lit. 186—188°), $[\alpha]_{red}^{20}$ −550° in $COMe_2$ [647—633 (640), 502—484 (493), 584, 524, 612, 541 mμ.] (*Zn* salt, m.p. 219°, $[\alpha]_{red}^{20}$ −630° in $COMe_2$ [620—608 (614), 508, 567, 534 mμ.]), with N_2H_4,H_2O, C_5H_5N, and NaOMe in MeOH at 115° gives the *form* (**IV**), m.p. 212—213°, *a* 0 (*Zn* salt, m.p. 204°, *a* 0), also obtained with some (**II**) from (**III**) by the same reagents at 115±2° and subsequent esterification. (**IV**) shows 2 active H, is unchanged by NH_2OH–Na_2CO_3–C_5H_5N at 100°, BzCl, $CHN_2{\cdot}CO_2Et$, HI–AcOH and then O_2, cold conc. H_2SO_4, boiling KOH–MeOH, or H_2–Pd–AcOH, but with conc. HCl at 100—110° (or boiling $NHPh_2$; spectroscopic evidence) gives (**II**). Deoxophyllerythrinhæmin-*a* Me ester with, successively, Na–*iso*-$C_5H_{11}{\cdot}OH$, $FeCl_3$–MeOH–Et_2O, and CH_2N_2 gives *mesodeoxopyroisophæophorbide*-a *Me ester*, m.p. 191° (Zn salt) [650—626 (638), 508—478 (493), 583, 524, 610, 541 mμ.], which with N_2H_4 etc. gives a substance, m.p. ~201° or 205°, having unchanged spectrum. Phyllochlorin Me ester with N_2H_4 etc. at 125° and then CH_2N_2 and sometimes H_2–Pd–$COMe_2$ gives *mesophyllochlorin Me* ester, m.p. 167° (and ? a *polymorph*, m.p. ~186°), *a* 0 (2 active H) (and phylloporphyrin and a chlorin), also obtained similarly [F. Baláž] from active mesophyllochlorin. Rhodochlorin or, less well, purpurin-7 Me_2 ester gives *mesorhodochlorin Me*$_2$ *ester*

(**V**), m.p. 196°, α 0 (2 active H; *Zn* salt, m.p. 206°, α 0 [644—618 (631), ~586, 510, 555 mμ.]). Pyrrochlorin with H_2–Pd in $COMe_2$ gives *mesopyrrochlorin Me ester*, m.p. 147°, $[\alpha]^{20}_{red}$ −460° in $COMe_2$ [642, 489, 590, 518, 614, 545 mμ.], or with N_2H_4 etc. gives the *form*, m.p. 172°, α 0 [same absorption]. Pyrroporphyrinhæmin with Na–*iso*-C_5H_{11}·OH–N_2 and then $FeCl_3$ give *isochlorin*-I, m.p. 186° (2 active H; unchanged by N_2H_4 etc.), and -II, m.p. 159°; -II is obtained also by hydrogenation of, best, porphyrin Me ester Zn salt; pyrroporphyrin and NaOEt at 200° give *iso*chlorin-II, -III, and -IV; these have very similar absorption [approx. 660—632 (646), 504—478 (491), 594, 521, 619, 546·5 mμ.]. N_2H_4,H_2O–C_5H_5N and (**I**) at 115° give a hydrazone, converted by HCl–MeOH into *mesopyrophæophorbide*-a *Me ester*, m.p. 234°, $[\alpha]^{20}_{red}$ −240° to −375° in $COMe_2$ [and a little (**I**)], also obtained by NaOMe–MeOH–C_5H_5N at 115° and then H_2–Pd–$COMe_2$. N_2H_4,H_2O–C_5H_5N at 100° and then HCl–MeOH does not affect the active form, m.p. 175°, $[\alpha]^{20}_{red}$ −525° to −660°, $[\alpha]^{20}_{white}$ −860° to −950° in $COMe_2$, of (**V**). NaOMe–MeOH–C_5H_5N at 0° does not affect mesophyllochlorin, $[\alpha]^{20}_{red}$ −560° to −730° in $COMe_2$.

The green ester amides obtained from purpurin-18 by bases (A., 1942, II, 181) are shown to be 6-carboxylamide 1-carbomethoxylates. Purpurin-18 Me ester (**VI**) and NH_2Et–C_5H_5N–H_2O and then CH_2N_2 give *chlorin*-p_6 *Me*$_2$ *ester* 6-*carboxylethylamide*, m.p. 226°, converted by NaOMe into *purpurin*-18 *Me ester ethylimide*, m.p. >280°. NH_3–H_2O–C_5H_5N at room temp. with (**VI**) gives *chlorin*-p_6 *Me*$_2$ *ester* 6-*carboxylamide*, m.p. 224°, and thence *purpurin*-18 *Me ester imide*, m.p. >270° [722—684 (703), 551—537 (544), 506, 479 mμ.], which resists methylation but with CHN_2·CO_2Et gives a substance [713—681 (697), 544—534 (539), 503, 547 mμ.]. Mesopurpurin-18 Me ester imide, m.p. 234° (lit. 241°) [705—675 (690), 544—534 (539), 509—497 (503), 632, 476, 656 mμ.], is similarly obtained. Mesopurpurin-18 Me ester oxime with BzCl–C_5H_5N–Et_2O gives the *benzoate*, m.p. 228°, rapidly hydrolysed by KOMe–MeOH at 200°. *Chlorin*-e_6 *Me*$_2$ *ester* 6-*carboxylethylamide* (from phæophorbide-*a*), m.p. 194°, *mesochlorin*-e_6 *Me*$_2$ *ester* 6-*carboxyl-amide* (15%), m.p. 194°, and *-piperidide* (from mesophæophorbide-*a*), m.p. 205°, are similarly obtained. *Mesorhodochlorin Me ester* 6-*carboxyl-piperidide* (**VII**), m.p. 186° [659—635 (647), 500—476 (488), 593, 617, 546, 518 mμ.], is obtained from mesorhodochlorinpropionic acid Me_1 ester by $POCl_3$–PCl_5 at 45°, followed by piperidine, and is unchanged by conc. H_2SO_4 or boiling KOH–Pr$^{\alpha}$OH. *Rhodoporphyrin Me*$_1$ *ester* 6-*carboxylpiperidide*, m.p. 260° [509—485 (497), 538—526 (532), 581—567 (567), 624 mμ.], is obtained by KOH–Pr$^{\alpha}$OH and then CH_2N_2 from (**VII**) or mesochlorin-p_6 Me_2 ester 6-carboxylpiperidide (prep. from the vinyl compound by H_2–Pd–$COMe_2$ and then $FeCl_3$), m.p. 194°. N_2H_4,H_2O–C_5H_5N at room temp. and then HCl–MeOH converts phyllochlorin Me ester into mesophyllochlorin Me ester, m.p. 149°. With N_2H_4,H_2O–C_5H_5N at 60° and then HCl–MeOH purpurin-7 Me_3 ester gives mesorhodochlorin Me_2 ester (poor yield), m.p. 171°, $[\alpha]^{20}_{red}$ −370° to −385° in $COMe_2$ (*Zn* salt, m.p. ~219°). R. S. C.

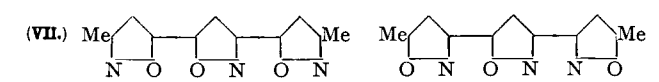
Chlorophylls. CXIII. Introduction of the acetyl group into 2-devinylpyrophæophorbide-*a*. Partial synthesis of vinylphæoporphyrin-a_5. H. Fischer and O. Oestreicher (*Annalen*, 1942, **550**, 252—260).—Figures in brackets below are absorption max. in Et_2O in order of intensity. Attempts to acetylate the Fe or *Zn* salt, m.p. 264° [643·6, 599·3, 562·5, 518·2, 490·1 mμ.], of devinylpyrophæophorbide-*a* by Ac_2O–$SnBr_4$ failed, but the amorphous *Cu* salt [641, 593, 503·1, 547 mμ.] gives a product, which with N_2H_4–AcOH and then HCl gives 2-*acetylpyrophæophorbide*-a, m.p. 242° [681, 508·7, 545·5, 631·9—614·2 mμ.], and some oxophyllerythrin. Vinyl*iso*chloroporphyrin-e_4-hæmin with hot $CHCl_2$·OEt (3 min.) and then Fe(OAc)$_2$–HCl–AcOH–H_2O gives 9-*hydroxy*-2-*hydroxyethyldeoxophæoporphyrin*-a_5 [see (**I**)] (~30%), cryst. [619·2, 500, 563·9, 534·5 mμ.], dehydrated at 305°, and oxidised, best by CrO_3–$COMe_2$–AcOH (little) or $K_2Cr_2O_7$–C_5H_5N, to 2-hydroxyethylphæoporphyrin-a_5 [561·2, 588·9, 521·7, 638·1 mμ.] and a small amount of another porphyrin. R. S. C.


(I.)

Heterocyclic compounds containing nitrogen. XLIX.—See A., 1942, II, 358.

[3-Methylthiazolone-2-*p*-aminobenzenesulphonimide.] K. A. Jensen (*Helv. Chim. Acta*, 1941, **24**, 1249—1250).—Comments on the publication of Hartmann and Druey (A., 1941, II, 271). H. W.

Tri*iso*oxazoles. C. Musante (*Gazzetta*, 1941, **71**, 172—182).—MgMeI (**I**) and 3-methyl*iso*oxazole-5-carboxyl chloride (**II**) in Et_2O, followed by dil. H_2SO_4, give 3-*methyl*-5-*iso*oxazolyldimethylcarbinol (**III**), b.p. 108—109°/8—9 mm., also obtained from Et 3-methyl-5-*iso*oxazolylcarboxylate (**IV**) and (**I**). MgEtI and (**II**) similarly give 3-*methyl*-5-*iso*oxazolyldiethylcarbinol, b.p. 132°/22 mm. When heated alone, or better with P_2O_5 or AcCl, (**III**) gives 3-*methyl*-5-*iso*propenyl*iso*oxazole, b.p. 100—105°/22 mm., oxidised by $KMnO_4$–H_2SO_4 to 3-methyl-5-*iso*oxazolyl Me ketone (**V**) (A., 1939, II, 523). A liquid mixture of (**IV**) and (**V**) with Na, followed by dil. H_2SO_4, gives 3 : 3′-*dimethyl*-5 : 5′-*di*isooxazolylmethane (**VI**), m.p. 180—181° (*Cu* salt). With conc. HCl, the dioxime, m.p. 212—214°, of (**VI**) gives 3′ : 3″-*dimethyl*-3 : 5-*di*-5′ : 5″-iso*oxazolyl*iso*oxazole* [3 : 3″-*dimethyl*-5 : 5′- 3′ : 5″-*tri*iso*oxazole*] (**VII**), m.p. 235°. With NHPh·NH_2


(VII.) (X.)

in boiling EtOH, (**VI**) gives 1-*phenyl*-3 : 5-(3′ : 3″-*dimethyldi*-5′ : 5″-iso*oxazolyl*)*pyrazole*, m.p. 154—155°. 5-Methyl-3-*iso*oxazolylcarboxylic acid gives an *Et* ester, b.p. 130°/33 mm., which with 5-methyl-3-*iso*oxazolyl Me ketone (**VIII**) and Na in Et_2O gives 5 : 5′-*dimethyl*-3 : 3′-*di*iso*oxazolylmethane*, m.p. 142° (*Cu* salt, decomp. 243°). With NH_2OH,HCl (**IX**), followed by conc. HCl, this gives 5′ : 5″-*dimethyl*-3 : 5-*di*-3′ : 3″-iso*oxazolyl*iso*oxazole* [5 : 5″-*dimethyl*-3 : 5′-3′ : 3″-*tri*iso*oxazole*] (**X**), m.p. 201°. With Na, (**IV**) and (**VIII**) give 3 : 5′-*dimethyl*-5 : 3′-*di*iso*oxazolylmethane*, m.p. 153—154° (*Cu* salt, decomp. ~250°), which with (**IX**) gives a *mixture*, not separated, of 3′ : 5″-dimethyl-5 : 3- and -3 : 5-di-5′ : 3″-*iso*oxazolyloxazole. E. W. W.

Structure-chemical investigations. III. Ammine-complexes with thiazole and dithiazolyl. H. Erlenmeyer and E. H. Schmid (*Helv. Chim. Acta*, 1941, **24**, 869—877).—The prep. of the following *salts* is described: α- and β-$CoCl_2$,2th (th = thiazole); $CoCl_2$,4th; Co[CNS]$_2$,4th. 4 : 4′-Dithiazolyl (=dith′) yields the *compounds*, [Ni dith′$_3$]Cl_2,6·5H_2O, $CuSO_4$ dith′,2H_2O, $CuSO_4$ dith′$_2$,5H_2O, whilst 2 : 2′-dithiazolyl (=dith″) gives the *substance*, $NiCl_2$ dith″,2H_2O. The following are described: $PtCl_2$ dith′; [Pt en dith′]Cl_2,H_2O; [Pt en dith′]I_2; [Pt dith′,NH_3]I; [Pt dith′$_2$]Cl_2,2H_2O; [Pt (dith′)$_2$]I_2. Comparison is made with the corresponding compounds of C_5H_5N and dipyridyl. H. W.

3-4′-Amino-2′-methyl-5′-pyrimidylmethyl-4-methyl-5-α-hydroxyethylthiazolium bromide hydrobromide, an isomeride of aneurin. P. Baumgarten, A. Dornow, K. Gutschmidt, and H. Krehl (*Ber.*, 1942, **75**, [*B*], 442—444).—Gradual addition of CH_2Cl·CO·CH_2Ac to HCS·NH_2 in abs. EtOH gives 5-*acetyl*-4-*methylthiazole* (**I**), b.p. 107—108°/13 mm., m.p. 28—29° [*hydrochloride*, m.p. 161° (decomp.); *picrate*, m.p. 108°; *methiodide*, m.p. 168°], also obtained from Et 4-methylthiazole-5-carboxylate, NaOEt, and EtOAc followed by treatment of the product with boiling 10% HCl. (**I**) is reduced by Al(OPr$^{\beta}$)$_3$ in Pr$^{\beta}$OH to 4-*methyl*-5-α-*hydroxyethylthiazole*, b.p. 146°/18 mm. (*methiodide*, m.p. 164·5°; *picrate*, m.p. 138°), which with 4-amino-2-methyl-5-bromomethylpyrimidine dihydrobromide gives 3-4′-*amino*-2′-*methyl*-5′-*pyrimidylmethyl*-4-*methyl*-5-α-*hydroxyethylthiazolium bromide hydrobromide*, m.p. 231° (decomp.); this does not exhibit true antineuritic action. H. W.

Ox-, thi-, and selen-azoles.—See B., 1942, II, 315, 318, 319, 348, 363, 366.

VII.—ALKALOIDS.

Identification of the alkaloids of tobacco by methylation of their picrates. A. Schmuk (*J. Appl. Chem. Russ.*, 1941, **14**, 864—866).—0·01—0·05 g. of the picrates of piperidine, nornicotine (**I**), or anabasine could be methylated quantitatively by heating with CH_2O–HCO_2H (cf. Späth *et al.*, A., 1935, 1136). Picric acid did not react with CH_2O–HCO_2H under the conditions used. The methylated alkaloids were identified by mixed m.p. (**I**) was thus identified in the following varieties of *Nicotiana*: *sylvestris, Palmeri, Benthamiana, trigonophylla, longiflora, suaveolens, inglubra, solanifolia*, and *sanguinea*. Determination of the m.p. of the picrate before and after methylation enabled (**I**) to be identified in presence of nicotine. The picrate of methylated salsoline could not be isolated (salsoline picrate, m.p. 191—193°); the *picrate* of methylated ammodendrine had m.p. 152—153°. N. G.

Compounds of hydrogenated nicotines. O. Hromatka (*Ber.*, 1942, **75**, [*B*], 522—530).—Hydrogenation of nicotine (**I**), even in the presence of a Pd catalyst, leads to rupture of the pyrrolidine ring whereas the C_5H_5N ring is not hydrogenated. (**I**) is reduced (Pd–C in H_2O at 54°) to dihydrometanicotine (**II**), b.p. 147°/20 Torr [*formyl*, b.p. 240—246°/35 mm., *Ac* (**III**), b.p. 164°/1 Torr, iso*valeryl*, b.p. 175°/1 Torr, and Bz, b.p. 215°/1 Torr (*H oxalate*, m.p. 88°; *hydrochloride*, m.p. 144°), derivatives]. (**II**) is transformed into its hydrochloride and heated at 160—170° with nicotinyl chloride hydrochloride, thus giving *nicotindihydrometanicotinamide*, b.p. 230°/0·5 Torr. (**II**) is converted by NEt_2·COCl into *diethylaminoformyldihydrometanicotine*, b.p. 174—177°/1 Torr, and by ψ-thiocarbamide Et ether hydrobromide into *guanyldihydrometanicotine* (*mono-* and *di-hydrobromide*; *dinitrate*). Octahydrometanicotine gives *diformyl*, b.p. 220—225°/3 Torr, *Ac*$_2$, b.p. 215°/1 Torr, *di*isovaleryl, b.p. 230° (bath)/0·5 Torr, Bz$_2$, b.p. 280° (slight decomp.)/1 mm., *diethylaminoformyl*, b.p. 218—226°/1 Torr, and *diguanyl*, m.p. 193°, derivatives. (**III**) when neutralised with N-HCl and then reduced (PtO_2 in H_2O at 68—72°) gives *monoacetyloctahydrometanicotine*, b.p. 170°/0·1 Torr; the *mono*isovaleryl, b.p. 180—195° (bath)/Torr, and *Bz*,

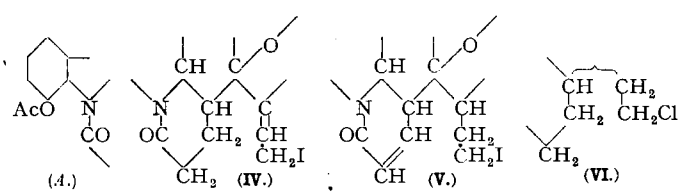
b.p. 210—230° (bath)/1 Torr, derivatives are obtained analogously. Nicotine dimethobromide is reduced to 3-δ-*dimethylaminobutylpyridine methobromide*, m.p. 118—120°, in presence of Pd–C and to NN′-*dimethyloctahydrometanicotine* (*dihydrobromide*, m.p. 216°) in presence of Pt. H. W.

Optical activities of some cinchona alkaloids and some of their salts in mixtures of water and ethyl alcohol. J. C. Andrews (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 543—545).—Data are presented on $[\alpha]_D^{25}$ of quinidine, cinchonine, dihydroquinidine, and conchonidine as free bases, sulphates, and hydrochlorides in H_2O–EtOH mixtures, and on the change of $[\alpha]_D^{25}$ as the free bases are progressively neutralised with H_2SO_4 and HCl. J. D. R.

Alkaloids of the *Colombo* root. VII. 2 : 3 : 11 : 12 : 13-Pentamethoxyberbine. E. Späth and T. Meinhard (*Ber.*, 1942, **75**, [*B*], 400—407).—3 : 4 : 5-Trimethoxyphenylacet-β-3′ : 4′-dihydroxyphenyl ethylamide (**I**), m.p. 100·5—101·5°, is obtained from 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}[CH_2]_2{\cdot}NH_2$ (**II**) and 3 : 4 : 5 : 1-$(OMe)_3C_6H_2{\cdot}CH_2{\cdot}CO_2H$ at 175° or, preferably, by adding Ag_2O to a mixture of (**II**) and 3 : 4 : 5 : 1-$(OMe)_3C_6H_2{\cdot}CON_2$ prepared from the chloride and CH_2N_2. (**I**) is readily converted by P_2O_5 in boiling PhMe into 6 : 7-*dimethoxy*-1-3′ : 4′ : 5′-*trimethoxybenzyl*-3 : 4-*dihydro*isoquinoline (**III**), m.p. 135—135·5° (vac.; slight decomp.) [*picrate*, m.p. 169—171° (decomp.)], reduced by Zn–Cu and dil. HCl to the *H*$_4$-*base* (**IV**), m.p. 101·5—102° (vac.) (m-*nitrobenzoyl* derivative, m.p. 141—142°). (**IV**) is converted by a large excess of CH_2O in MeOH at 100° into an unidentified base, m.p. 185—185·5° (vac.). With less CH_2O in MeOH at room temp. (**III**) gives 2 : 3 : 11 : 12 : 13-*pentamethoxyberbine*, m.p. 148—149° (vac.; slight decomp.), which gives a berbinium iodide when heated with I–EtOH. (**III**) is dehydrogenated by Pd-sponge at 200° to 6 : 7-*dimethoxy*-1-3′ : 4′ : 5′-*trimethoxybenzyl*isoquinoline, m.p. 152·5—153·5° (*picrate*, m.p. 185—186°). H. W.

Constitution of anolobine. T. R. Govindachari (*Current Sci.*, 1942, **11**, 238).—Treatment of *dl*-2-methoxy-5 : 6-methylenedioxynoraporphine (A., 1941, II, 272) with $ClCO_2Et$ and alkali gave a *product*, m.p. 169—170°, different from the *product*, m.p. 245—247°, similarly obtained from anolobine *O*-Me ether; anolobine cannot therefore have the constitution assigned by Manske (A., 1938, II, 298). H. A. P.

Constitution of *Strychnos* alkaloids. XXVII. *iso*- and Deoxyvomicine. H. Wieland and M. Thiel (*Annalen*, 1942, **550**, 287—300; cf. A., 1942, II, 39).—Transformation of vomicine (**I**) into *iso*vomicine (**II**) by red P–HBr–AcOH is reversible, which supports the view that the change (**I**) → (**II**) involves opening of the oxide ring B. With boiling 20% KOH–MeOH–N_2, (**II**) gives *iso*vomicic acid, which probably lactonises at the m.p. [256° (decomp.) after sintering at 239°]. In AcOH, (**II**) absorbs 3·5 H_2 (PtO_2), giving bases, $C_{22}H_{30}O_2N_2$, m.p. 210°, and (?) $C_{22}H_{26}O_3N_2$, m.p. ~240—247°. Electrolytic reduction of (**II**) gives *isovomicidine*, $C_{22}H_{26}O_3N_2$, sinters at 240°, m.p. 290° (decomp. from 260°) (H sulphate). With Ac_2O–NaOAc at 100°, (**II**) gives a *mono*-, m.p. 191—192° (sole product by Ac_2O–C_5H_5N at 100°), and *di*-*acetate*, m.p. 173°, and (**I**) gives a *monoacetate*, m.p. 204—205° [hydrolysis regenerates (**I**)]; structures involve (*A*). Deoxyvomicine (**III**) (yellow or white) does not contain 2 OH as it gives only a *monoacetate*, m.p. 220°. Red P–HI–AcOH at the b.p. converts (**I**) or (**II**) into a base, $C_{22}H_{25}O_3N_2I$



(*A*.) (**IV**.) (**V**.) (**VI**.)

(? **IV**), m.p. 223° (decomp.), and a mixture, reduced by Zn–AcOH to (**III**). The corresponding base from dihydrovomicine is probably (**V**). Boiling P–H_3PO_4–KI converts (**II**) into (**III**) (60%) and (**I**) into *neodeoxyvomicine* (20%), m.p. 312° (decomp. from 300°) (with H_2–PtO_2–AcOH gives a H_2-derivative, m.p. 321°). $SnCl_2$–HCl at 125° or boiling HBr–P–AcOH has no effect on (**III**). With $SnCl_2$ and HCl at 130°, (**I**) gives a *base*, $C_{22}H_{25}O_3N_2Cl$ (? **VI**), m.p. 245°(decomp.). R. S. C.

Strychnos **alkaloids. CXV. Behaviour of strychnine and *iso*strychnine towards hydrobromic acid.** H. Leuchs and H. Schulte (*Ber.*, 1942, **75**, [*B*], 573—579).—Strychnine is converted by red P in boiling AcOH–HBr (*d* 1·78) followed by addition of $KHCO_3$ or NaOH into a complex bromodeoxy*iso*strychnine, $(C_{21}H_{21}ON_2Br)_x$, becomes discoloured at 220° and very dark at 290—300°, which is isolated as the *hydrobromide* (**I**) when the acid solution is cooled. Boiling N-HBr hydrolyses (**I**) to *iso*strychnine, m.p. 223—224° (vac.), $[\alpha]_D^{18}$ +27·6° in abs. EtOH. (**I**) is hydrogenated (PtO_2 in AcOH) to *tetrahydrodeoxy*iso*strychnine*, m.p. 174—176° (vac.) or (hydrated) softens at 90—110°, re-solidifies and has m.p. >170° [*perchlorate*, m.p. 143—145° (decomp.) or (dried) m.p. 160—170° to a clear resin]. (**I**) is converted by Zn dust in AcOH–HBr (*d* 1·78) into *deoxy*iso*strychnine*, m.p. 195—197° (vac.), softens at 115°. Bromodihydro*iso*strychnine, m.p. 280°, and deoxydihydro*iso*strychnine (*perchlorate*, m.p. 175°) are described. Dihydrostrychnine dimethosulphate is converted by red P–HBr–AcOH into a compound [*perchlorate*, $C_{21}H_{25}ON_2Br,HClO_4$, m.p. 260—261° (block)]. H. W.

Alkaloids of lycopodium species. II. Degradation experiments with lycopodine. L. Marion and R. H. F. Manske (*Canad. J. Res.*, 1942, **20**, **B**, 153—156).—Se-dehydrogenation of lycopodine (**I**) affords a mixture of five bases, including 7-methyl- (**II**) and 5 : 7-dimethyl-quinoline. (**II**) is also obtained by heating (**I**) with Pd–$BaSO_4$ or *o*-$C_6H_4(CO)_2O$ at 250° for 7 hr. (**I**) probably contains a fully hydrogenated quinoline nucleus. The O may be present as a cyclic ether. W. C. J. R.

VIII.—ORGANO-METALLIC COMPOUNDS.

Sulphophenylarsinic acids and their derivatives. VI. Derivatives of *p*-sulphonamidophenylarsinic acids. E. L. Way and J. F. Oneto (*J. Amer. Chem. Soc.*, 1942, **64**, 1287—1288; cf. A., 1942, II, 158).—By standard methods *p*-$AsO_3H_2{\cdot}C_6H_4{\cdot}SO_2Cl$ leads to p-*arsinophenylsulphon-dimethyl*-, -p-*xenyl*-, and -N-*phenyl*-N-*benzyl-amide*, -*morpholide*, and -*piperidide*, and the corresponding AsI_2 compounds, m.p. 98—99°, 146—147°, 154—156°, 167·5—169·5°, and 127—129°. p-*Arsinoxidophenylsulphon-dimethyl*- and -p-*xenyl-amide*, -*morpholide*, m.p. 196—197°, and -*piperidide*, m.p. 194—195·5°, and p-*arsenophenylsulphon-dimethyl*- and -N-*phenyl*-N-*benzyl-amide* are described. R. S. C.

Arsenobenzenes.—See B., 1942, II, 316.

Mercury ethyl phosphate. N. N. Melnikov and M. S. Rokitskaja (*J. Appl. Chem. Russ.*, 1941, **14**, 446—448).—$(HgEt)_3PO_4$ (**I**) is obtained in 96—99% yield by heating and stirring $HgEt_2$ and $Hg_3(PO_4)_2$ with 10% of H_2O to 80—100° for 40—70 min. Apparatus for the large-scale production of (**I**) is suggested. G. A. R. K.

Mercuri-compounds.—See B., 1942, III, 223.

IX.—PROTEINS.

Fractionation of gelatin. R. Signer and H. Mosimann (*Helv. Chim. Acta*, 1941, **24**, 1058—1067).—Air-dried gelatin (**I**) is degraded by prolonged boiling with H_2O and pptd. in fractions from the solution by gradual addition of EtOH at room temp. The first fractions give elastic films but this property is missing from the later fractions. The first absorb small amounts of H_2O and swell whereas the last rapidly give a viscous solution. The colour of the fractions varies continuously. The fractionation of undegraded (**I**) by EtOH from solutions in 4M-$CO(NH_2)_2$ is described. H. W.

Chromatographic separation of the cleavage products of clupein. E. Waldschmidt-Leitz, J. Ratzer, and F. Turba (*J. pr. Chem.*, 1941, [ii], **158**, 72—78).—The products obtained from clupein by pancreas proteinase at p_H 8 are separated by adsorption from H_2O on fuller's earth into fractions having N/NH_2 ratios ~17, ~9, and ~5, unchanged by further chromatography. The absorption is governed by the no. of arginine residues in the cleavage products and not by the mol. wt. Similarly the absorbability of arginine is the same as that of glycylarginine, but is ≫ that of leucylglycine or leucylglycylglycine. R. S. C.

Liberation of free amino-nitrogen from proteins in the Van Slyke apparatus. F. Lieben and Y. C. Loo (*J. Biol. Chem.*, 1942, **145**, 223—228).—An estimate of the quantity of lysine combined in the protein can be obtained by measurement of the quantities of N_2 liberated after 30, 60, and 90 min. respectively by the combined action of HNO_2 on intact proteins in the volumetric Van Slyke apparatus. Comparison of the curve for the rate of liberation of N_2 from casein with those obtained for zein, arginine, salmine, and guanidine suggests that the apparently unimol. nature of the reaction by which the extra amino-N is evolved after liberation of the ε-NH_2-N of lysine may be ascribed to the arginine present in the protein which acts by partial decomp. of the guanidino-group. H. W.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Adipic acid as an oxidation product of the diaminocarboxylic acid derived from biotin. K. Hofmann, D. B. Melville, and V. du Vigneaud (*J. Biol. Chem.*, 1942, **144**, 513—518; cf. A., 1942, II, 242).—The diaminocarboxylic acid, $C_9H_{18}O_2N_2S$, previously obtained from biotin and $Ba(OH)_2$ at 140°, is oxidised by alkaline $KMnO_4$ at room temp., or by HNO_3 (*d* 1·42) to give adipic acid (**I**). Biotin Me ester and N_2H_4,H_2O at 130° afford a *hydrazide*, $C_{10}H_{18}O_2N_4S$, m.p. 238—240°, converted by $NaNO_2$–HCl into the azide, and thence

(boiling EtOH) into the *ethylurethane* (II), $C_{12}H_{21}O_3N_3S$, m.p. 188—190°. (II) is hydrolysed by $Ba(OH)_2$ to a *triamine* (III), $C_9H_{19}N_3S$ [*sulphate*, $(C_9H_{19}N_3S)_2,3H_2SO_4,2H_2O$, m.p. 249—252° (decomp.); *tripicrolonate*, decomp. 250°; *tribenzoate*, m.p. 194—195°]. (II) and conc. HCl at 100° give a *monoamine*, $C_9H_{17}ON_3S$ [*hydrochloride*, m.p. 265—270° (decomp.)], and thence $[Ba(OH)_2]$ (III). As (I) is not obtained by oxidising (III), one CO_2H in (I) is the original CO_2H in biotin. A. T. P.

Hydrolysis of biotin sulphone. D. B. Melville, K. Hofmann, and V. du Vigneaud (*J. Biol. Chem.*, 1942, **145**, 101—105).—The diaminocarboxylic acid sulphate, obtained from biotin by hydrolysis with $Ba(OH)_2$, is converted by Ac_2O and NaOH into its Ac_2 derivative, m.p. 187—189°, oxidised by H_2O_2 in AcOH to the corresponding *sulphone*, m.p. 209—211°. This is hydrolysed by conc. HCl at 120° to the diaminocarboxylic acid sulphone, m.p. 142—152°, identical with the compound obtained by Kögl and de Man (*Z. physiol. Chem.*, 1941, **269**, 81) by the hydrolysis of biotin sulphone (I) by conc. HCl at 200° and regarded by them as a 9-C diaminocarboxysulphonic acid. Its constitution is established by its conversion by $COCl_2$ and Na_2CO_3 into (I), m.p. 273—275°. H. W.

Aloins. Formation of formaldehyde and furfuraldehyde. J. H. Gardner and J. A. Campbell (*J. Amer. Chem. Soc.*, 1942, **64**, 1378—1379).—CH_2O and a pentose (furfuraldehyde test) are obtained when aloin is heated with (*a*) borax and then with HCl or (*b*) perborate (no acid necessary), but not by borax or HCl alone (cf. Cahn *et al.*, A., 1932, 1252; Goldner., B., 1932, 863). R. S. C.

Polarographic determination of citrinin. H. W. Hirschy and P. M. Ruoff (*J. Amer. Chem. Soc.*, 1942, **64**, 1490—1491).—Citrinin (from *Penicillium citrinum*), m.p. 170—171°, is reduced at a dropping Hg cathode in 0·001—0·003M. solution in 75% EtOH, buffered or unbuffered, or in 0·1N-KCl–75% EtOH, but not in NaOAc–EtOH (p_H 6·0) or PO_4'''–EtOH (p_H 7·4). In EtOH at p_H 2·05 the half-wave potential is −0·80 to −0·82 v. Potentiometric reduction by $TiCl_3$ is impracticable. (I) has k 5·5 × 10^{-4} in 95% EtOH at 21°. Colour changes are: p_H <4·6, lemon-yellow (green fluorescence); p_H 4·6, begins to fade; p_H 5·6—5·8, change to orange-pink; p_H >9·9, cherry-red. R. S. C.

XI.—ANALYSIS.

Differentiation of substances mixtures of which do not show a marked depression of m.p. L. Kofler and M. Brandstätter (*Ber.*, 1942, **75**, [*B*], 496—502).—Substances which do not show a marked depression of mixed m.p. by reason of non-miscibility of the liquid phases can be differentiated by the appearance of different molten particles when viewed under the microscope, and by observation of the eutectic temp. when mixed with other substances and of the refractive index of the liquids determined on the glass powder scale. When the abscnce of m.p. depression depends on the formation of mixed crystals, the microscopic technique and the use of isomorphous substances is ineffective. In this case the contact method (with re-melting if necessary) and determination of refractive index give the desired information. H. W.

Determination of volatility of organic substances.—See A., 1942, I, 357.

Solvent for determination of mol. wt. according to Rast.—See A., 1942, I, 358.

Identification of alcohols by means of optical properties of esters of carbanilic acid. B. T. Dewey and N. F. Witt (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 648; cf. A., 1940, II, 360).—The phenylurethanes of the following alcohols have been prepared and their m.p. and optical crystallographic data recorded; $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, *iso*-$C_5H_{11}{\cdot}OH$, borneol, $Bu^{\beta}OH$, $C_{16}H_{33}{\cdot}OH$, $CHPh{:}CH{\cdot}CH_2{\cdot}OH$, *cyclo*hexanol, $CHEt_2{\cdot}OH$, $CH_2Br{\cdot}CH_2{\cdot}OH$, $CH_2Cl{\cdot}CH_2{\cdot}OH$, $(CH_2{\cdot}OH)_2$, furfuryl alcohol, menthol, p-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$, $CH_2Ph{\cdot}CHMe{\cdot}OH$, 2-, 3-, 4-methyl*cyclo*hexanol, $CHMePr^{\beta}{\cdot}OH$, myristyl alcohol, $Pr^{\beta}OH$, terpineol, and tetrahydrofurfuryl alcohol. The optical properties provide a means of identifying the urethanes even when they are mixed with $CO(NHPh)_2$. J. D. R.

Spectro-photometric determination of small amounts of acetone. H. L. J. Bäckström (*Z. anal. Chem.*, 1942, **123**, 96—112).—The solution containing $COMe_2$ (2 c.c.) is treated with aq. KOH (100 g. of KOH in 60 c.c. of H_2O) (2 c.c.) and a 10% solution of vanillin in MeOH (1 c.c.) and heated to 50—65° during 20 min. After adding H_2O (10 c.c.) the colour is compared photometrically with standards, preferably using an S50 or S47 filter. With the filter MeCHO has little effect and CH_2O no effect on the results. Applications of the method to the determination of $COMe_2$ in milk and to the determination of citric acid by conversion into $COMe_2$ are described. J. W. S.

Chromatometric determination of glucose. S. T. Orlovski (*J. Appl. Chem. Russ.*, 1941, **14**, 671—673).—1—10 c.c. of 0·1—2% glucose solution mixed with 4—8 c.c. of 7—13% $K_2Cr_2O_7$ and 25 c.c. of 15N-H_2SO_4, are kept at 80—90° for 70 min.; then the excess of $K_2Cr_2O_7$ is titrated with $FeSO_4$. J. J. B.

Identification of sugars by microscopic appearance of crystalline osazones. W. Z. Hassid and R. M. McCready (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 683—686).—Photomicrographs of the osazones of hexoses and pentoses are given, with details of procedure for prep. of osazones for microscopical identification by comparison with the photographs presented. J. D. R.

Determination of β-carotene and neo-β-carotene with the visual spectrophotometer. F. P. Zscheile and B. W. Beadle (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 633—634).—β-Carotene and neo-β-carotene can be determined in purified solutions from spinach extracts by a visual spectrophotometer. The total carotene is calc. from the absorption at 4358 A. and the % of either from the absorptions at 4358 and 4916 A. J. D. R.

Determination of small amounts of benzene in the presence of *cyclo*hexane, and of toluene in presence of methyl*cyclo*hexane. B. B. Corson and L. J. Brady (*Ind. Eng. Chem.* [*Anal.*], 1942, 14, 531—533).—The mixture of C_6H_6 in C_6H_{12} (C_6H_6 >12%) is mixed with H_2SO_4–HNO_3, and the ΔT of the nitration reaction is measured under standard conditions of stirring and timing. The C_6H_6 content is read from a preformed calibration graph connecting ΔT with % C_6H_6. If the $[C_6H_6]$ is >12% the mixture is diluted with pure C_6H_{12}. PhMe in C_7H_{14} is determined in the same way. The average deviation from the mean is 0·06%. J. D. R.

Sulphanilamide, sulphapyridine, sulphathiazole, sulphaguanidine, and sulphadiazine. Assay, differentiation, and identification. J. A. Calamari, R. Hubata, and P. B. Roth (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 534—535).—The drugs are identified by m.p., solubility in H_2O, 5% HCl, 5% NaOH, Et_2O, and $COMe_2$, colour of diazonium chloride, and reaction with $SnCl_2$–HCl. Assay is carried out by titration with 0·1N-$NaNO_2$. J. D. R.

Attempted use of dyes as " indicators " in the bromometric determination of organic compounds. W. Bielenberg (*Ber.*, 1942, 75, [*B*], 686—691).—Attempts are described to determine PhOH and *o*-, *m*-, and *p*-cresol by titration with KBr–$KBrO_3$ in acid solution in presence of fast-red V, ponceau 2R, Me-orange, azofuchsin 6B, neutral-red, alizarin-saphirol, or crocein-scarlet. These are unsuccessful since both substance and " indicator " react with $KBrO_3$ although at different rates and decolorisation or change of colour depends on the amount of substance and of dye. H. W.

Detection and determination of 4-amino-2-methyl-1-naphthol. Synthetic vitamin-*K*. A. R. Menotti (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 601—602).—The solution of 4 : 2 : 1-$NH_2{\cdot}C_{10}H_5Me{\cdot}OH$ (I) diluted to ~1 mg. per ml. is mixed with a solution of $Na_3[Fe(CN)_5NH_3]$ and the resulting blue colour is compared colorimetrically with a standard. 5 × 10^{-5} g. of (I) can be detected. J. D. R.

Applications of the bromometric assay. I. Bromination of derivatives of aminobenzoic acids.—See A., 1942, II, 360.

Determination of the concentration of solutions by a system of two solvents. III. Determination of moisture in organic compounds insoluble in water. S. I. Spiridonova (*J. Appl. Chem. Russ.*, 1941, **14**, 646—651).—If a solution of dry camphor (I) (or borneol, or a similar substance) in EtOH requires a_1 c.c. of H_2O to produce turbidity, a solution of (I) containing c% of H_2O requires a_2, and a solution of (I) containing x% of H_2O requires a, $x = c(a - a_1)/(a_2 - a_1)$. J. J. B.

Colorimetric determination of phenothiazine with palladous chloride. L. G. Overholser and J. H. Yoe (*Ind. Eng. Chem.* [*Anal.*], 1942, **14**, 646—647).—The phenothiazine (I) in $COMe_2$–H_2O is treated with $PdCl_2$ in NaOAc–HCl and the colour produced compared with known standards in Nessler tubes. The blue colour is due to the formation of a complex $C_{12}H_9NS,PdCl_2$ (prep. described), which is extracted by EtOAc from H_2O, giving a red solution. The red EtOAc solution is less stable than the blue solution in aq. $COMe_2$ and is not suitable for determination of (I). J. D. R.

Analytical classes of cannabinol compounds in marihuana resin.—See A., 1942, III, 771.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

DECEMBER, 1942.

I.—ALIPHATIC.

Catalytic alkylation of hydrocarbons.—See B., 1942, II, 306.

Ionisation and dissociation by electron impact: ethane, *n*- and *iso*-butane.—See A., 1942, I, 404.

Catalytic isomerisation of *n*-heptane.—See A., 1942, II, 306.

Structure of substituted ethylenes and their isomerisation polymerisation and "peroxide addition" reactions.—See A., 1942, I, 353.

Action of sulphur trioxide and oleum on chloroform.—See A., 1942, I, 406.

Chlorobromofluoromethane. K. L. Berry and J. M. Sturtevant (*J. Amer. Chem. Soc.*, 1942, **64**, 1599—1600).—CHClBrF, m.p. −115° (corr.), b.p. 36·11—36·18° (corr.)/756—756·2 mm. [unstable digitonide, *a* 0—0·15° (*l* = 1)], is obtained by the reactions, CH_2:CH·OAc + Cl_2 in EtOH → $CH_2Cl·CH(OEt)_2$ → (Br, hydrolysis) $CHClBr_2$ → (Br–SbF_3) CHClBrF (~25%). Its resolution may (preliminary experiments) be possible by way of additive compounds with optically active compounds. R. S. C.

Production of nitrohydrocarbons.—See B., 1942, II, 306.

Rate and mechanism in the reactions of *tert.*-butyl nitrate and of benzyl nitrate with water and with hydroxyl ion.—See A., 1942, I, 401.

Hydration of *iso*butene in dilute nitric acid.—See A., 1942, I, 401.

Manufacture of unsaturated alcohols.—See B., 1942, II, 307.

Syntheses involving utilisation of magnesium allyl bromide in the Grignard reaction.—See A., 1942, II, 430.

Photochemical production of branched carbon chains from ether and formaldehyde. R. Pummerer, H. Hahn, F. Johne, and H. Kehlen (*Ber.*, 1942, **75**, [*B*], 867—881).—The solutions are obtained by agitating 30—32% CH_2O with Et_2O and drying with freshly ignited Na_2SO_4, after which they contain CH_2O as the hydrate, or by passing gaseous CH_2O into the well-cooled Et_2O. After exposure to sunlight in presence of $COPh_2$ they contain benzpinacol, pentaglycerol (**I**), m.p. 200° (*triacetate*, b.p. 161—162°/15 mm.), β-methyltrimethylene glycol (**II**), b.p. 75—76°/0·3 mm. (*diacetate*, b.p. 61—63°/0·5 mm.; *di*-m-*nitrobenzoate*, m.p. 116°), and an oil (**III**), b.p. 75—85°/0·3 mm., which rapidly reduces Fehling's solution. (**I**) does not react with $Pb(OAc)_4$. (**II**) is oxidised by 5% HNO_3 at room temp. to $CHMe(CO_2H)_2$. (**III**) contains $CHMe(CHO)_2$, identified as the *di*-3 : 5-*dinitrophenylhydrazone*, m.p. 294°, and *hydroxyacetone*, b.p. 51—53°/20 mm. It is assumed that H required for the formation of (**I**) and (**II**) is obtained by dehydrogenation of EtOH resulting from Et_2O and possibly in part of the direct dehydrogenation of Et_2O. Irradiation of solutions of CH_2O in $Bu^{\alpha}{}_2O$ leads to *β-propyltrimethylene glycol* (*diacetate*, b.p. 73—75°/0·05 mm.) and $CPr^{\alpha}(CH_2·OH)_3$ (*triacetate*, b.p. 136—140°/0·1 mm.). The suggested course of the change is: $Et_2O + CH_2O$ → OEt·CHMe·CH_2·OH → (+CH_2O) OEt·CMe(CH_2·OH)$_2$ → $CHMe(CH_2·OH)_2$ → $CMe(CH_2·OH)_3$ ← $(OH·CH_2)_2CMe·CHO$ + EtOH. H. W.

Utilisation of aliphatic nitro-compounds. IV. Nitro-diols from simple aldehydes. C. A. Sprang [with E. F. Degering] (*J. Amer. Chem. Soc.*, 1942, **64**, 1735—1736; cf. A., 1942, II, 295).—Addition of EtCHO (130) to $MeNO_2$ (61) and K_2CO_3 (3 g.) (not NaOH) in 95% EtOH at 28—35° and keeping at room temp. for 4 days gives 50% of *δ-nitro*-n-*heptane-γε-diol*, m.p. 97°. Condensation (K_2CO_3–EtOH) of $MeNO_2$ with EtCHO and then MeCHO gives *γ-nitro*-n-*hexane-βδ*-, m.p. 94°, and with *n*-C_6H_{13}·CHO gives *θ-nitro*-n-*pentadecane-ηι-diol*, m.p. 66—67°. R. S. C.

Constitution of mannito-zirconic and -ferric acids.—See A., 1942, I, 405.

Crystalline xylitol. M. L. Wolfrom and E. J. Kohn (*J. Amer. Chem. Soc.*, 1942, **64**, 1739).—H_2–Ni–kieselguhr converts *d*-xylose in H_2O at 150°/160 atm. into xylitol, m.p. 61—61·5° (corr.) (lit., a syrup), $[\alpha]_D$ ±0 [penta-acetate, new m.p. 62·5—63° (corr.); $(CHPh{:})_2$ derivative, new m.p. 187·5—188° (corr.); consumes 4·0 $NaIO_4$ giving 2·8 HCO_2H and 1·8 CH_2O]. R. S. C.

αβγδ-Dibenzylidene-*D*-sorbitol. J. K. Wolfe, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 1493—1497).—*D*-Sorbitol with 2 mols. of PhCHO gives a mixture containing a $(CHPh)_3$ derivative, but with 1·1 mol. in conc. HCl–H_2O (1 : 2) at room temp. gives a powder, converted by BzCl–C_5H_5N at room temp. into *αβγδ-dibenzylidene*-D-*sorbitol εζ-dibenzoate* (**I**), m.p. 195—196°, $[\alpha]$ −41·5° in $CHCl_3$. NaOMe–$CHCl_3$–MeOH hydrolyses (**I**) to *αβγδ-dibenzylidene*-D-*sorbitol* (**II**), cryptocryst., m.p. 219—221°, $[\alpha]$ +21·6° in C_5H_5N, the structure of which is proved as follows. With Ac_2O–C_5H_5N at 100°, (**II**) gives the *εζ-diacetate*, m.p. 202—205°, $[\alpha]$ +4·1° in $CHCl_3$, hydrolysed by NaOMe to (**II**). In C_5H_5N at 0° (later 15°), (**II**) gives the *εζ-di*-p-*toluenesulphonate*, m.p. variable, 155—156° to 159—160°. In C_5H_5N at room temp., (**II**) gives the *ζ-CPh$_3$ ether*, dimorphic, m.p. 110—115° and 182—183°, $[\alpha]$ +16·8° in EtOAc (*ε-acetate*, m.p. 117—119°, resolidifies, remelts at 186—187°, $[\alpha]$ −41·8° in EtOAc, −46·5° in $CHCl_3$). Ac_2O–AcOH containing a little H_2SO_4 converts (**I**) into D-*sorbitol εζ-dibenzoate αβγδ-tetra-acetate*, m.p. 96—97°, $[\alpha]$ +14·4° in $CHCl_3$. (**II**) consumes rapidly 1 equiv. of $Pb(OAc)_4$ in AcOH and slowly a further 4 equivs.; use of 1·1 equiv. at <25° leads to CH_2O and aldehydo-2 : 3 : 4 : *5-dibenzylidene*-L-*xylose*, m.p. 186—187°, $[\alpha]$ −33·4° in C_5H_5N (*oxime*, m.p. 239—240°, $[\alpha]$ −108·9° in C_5H_5N), isolated by conversion by warm MeOH–$CHCl_3$ into the *Me hemiacetal* (**III**), m.p. 187—188°, $[\alpha]$ +40·4° in C_5H_5N, and obtained therefrom by sublimation at 140—145°/vac. HCl–MeOH–H_2O hydrolyses (**III**) to *L*-xylose, m.p. 143—145°, $[\alpha]$ −92° → −19·4° in H_2O, the structure of which is proved by admixture with *D*- to give *DL*-xylose, m.p. 128—130°, $[\alpha]$ ±0° in H_2O, of its phenylosazone, m.p. 161—163°, with the *D*-isomeride to give the *DL*-phenylosazone, decomp. 207°, $[\alpha]$ ±0° in C_5H_5N, and of its phenylosazone triacetate, m.p. 116—117°, $[\alpha]_D$ +44·3° in $CHCl_3$, with the *D*-isomeride, $[\alpha]$ −44·2° in $CHCl_3$, to give the *DL*-compound, m.p. 131—132°, $[\alpha]$ ±0° in $CHCl_3$. M.p. are corr. $[\alpha]$ are $[\alpha]_D^{20}$. R. S. C.

Structure of αγδζ-di-*o*-nitrobenzylidenedulcitol. R. M. Hann, W. T. Haskins, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 1614—1615).—Dulcitol and *o*-NO_2·C_6H_4·CHO give *αγδζ-dibenzylidenedulcitol*, m.p. 261—262° (*βε-diacetate*, m.p. 320—321°, and *-di*-p-*toluenesulphonate*, decomp. 221—222°) (cf. Tanasescu *et al.*, A., 1934, 169), the structure of which is proved by its resistance to $Pb(OAc)_4$–AcOH and conversion of its dibenzoate, m.p. 320—321°, by H_2SO_4–Ac_2O–AcOH at 20° into dulcitol *βε*-dibenzoate *αγδζ*-tetra-acetate, m.p. 157—158°. M.p. are corr. R. S. C.

Production of nitrohydroxy-compounds and nitro-alcohols.—See B., 1942, II, 308.

Higher unsaturated thiols and their derivatives. T. Lennartz (*Ber.*, 1942, **75**, [*B*], 833—853).—*Oleyl thiol* (**I**), b.p. 177—178°/0·2 mm. (p-*nitrobenzoate*, m.p. 50°), is prepared from oleyl bromide, NaOMe in abs. MeOH, and H_2S at room temp., then at 70—80°, and finally at 100° or by reduction of oleyl thiocyanate by Zn–Hg and HCl and purified through the Pb salt. Similarly obtained are *chaulmoogryl thiol*, b.p. 183—199°/0·2 mm. (converted by CHPh:CH·COCl at 80°, then 120°, and finally 140—150°, into the *cinnamate*, m.p. 43—48°), and *cinnamyl thiol*, b.p. 116—118°/0·1 mm. Thioethers are obtained from the requisite alkyl halides and Na alkyl mercaptides under N_2 in xylene or, better, abs. EtOH, the Na compounds being obtained from the thiol and Na in boiling xylene or by use of a solution of Na in EtOH. The following *sulphides* are described: *Et oleyl*, b.p. 191—195°/0·3 mm.; *oleyl CH_2Ph*, b.p. 250°/0·2 mm.; *CH_2Ph chaulmoogryl*, b.p. 234°/0·05 mm.; *cinnamyl chaulmoogryl*, b.p. 250—260°/0·4 mm.; *cinnamyl hydnocarpyl*, b.p. 228—232°/0·03 mm.; *dioleyl*, b.p. 260—280°/0·5 mm., m.p. 43—45°, and *diisohydnocarpyl*, m.p. 47—48°. The thioethers delay the development of leprosy in rats but the therapeutic activity is probably < that of the thiocyanates. *Et oleyl*, b.p. 184—190°/0·2 mm., *CH_2Ph oleyl*, b.p. 198—204°/0·075 mm., *cinnamyl oleyl*, b.p. 230—250°/0·1 mm., and *cinnamyl chaulmoogryl*, b.p. 252—263°/0·02 mm., *ether* are therapeutically inactive. Passage of HCl into a solution of glucose and (**I**) in abs. EtOH at −7° to +2° gives *glucose dioleyl mercaptal*, m.p. 104°, in ~25% yield. Oleyl bromide and $CS(NH_2)_2$ in abs. $COMe_2$ at 100° yield *oleylisothiocarbamide hydrobromide* (**II**), m.p. 108—109° (the free *base*, m.p. 83°, gives a yellow Pb mercaptide with Na plumbite in cold $COMe_2$ and is decomposed by boiling 2N-NaOH into NH_3 and a *compound*

$C_{18}H_{36}O_2S$, m.p. 48°). Similarly obtained are *hydnocarpyl-*, m.p. 108—110°, and *chaulmoogryl-*isothiocarbamide *hydrobromide*, m.p. 117—118° (*base*, m.p. 83—85°), and *octadecyl*isothiocarbamide *hydrochloride*, m.p. 132° (free *base*, m.p. 89—91°). *N-Acetyl-S-oleyl*isothiocarbamide, m.p. 118°, is obtained from (**II**) and AcCl in boiling C_6H_6. *p*-NHAc·C_6H_4·SO_2Cl and (**II**) in boiling PhMe containing $SnCl_4$ afford N-p-*acetamidobenzenesulphonyl*-S-*oleyl*isothiocarbamide, m.p. 107°, which could not be hydrolysed to the free base. *Oleylthiourethane*, m.p. 103—104·5°, is obtained from oleyl thiocyanate and HCl–MeOH at 0°, from (**I**) and $COCl_2$ followed by NH_3, and from (**II**) and 30% H_2O_2 in 100% AcOH at room temp. *Hydnocarpyl-*, m.p. 93—94°, $[\alpha]_D$ +34·76° in $CHCl_3$, *chaulmoogryl-*, m.p. 102°, and *octadecyl-*, m.p. 108·5—109°, *-thiourethane* are described. *Chaulmoogryl chlorothioformate*, b.p. 200—203°/1 mm., is obtained from $COCl_2$ and the thiol at 95°. *Cinnamyl*-N-*oleylxanthamide*, m.p. 98—99°, obtained from oleylthiocarbimide and CHPh:CH·CH_2Br in boiling 99% EtOH, gives a ppt. of PbS with warm Na plumbite. Oleyl bromide is transformed by Na_2SO_3–H_2O in a Cu autoclave at 160—170° into *Na oleylsulphonate*, sinters at 135°, softens without completely melting at 155°, and becomes discoloured at 200°, converted by successive treatments with $POCl_3$ at 100° and NH_3 into *oleylsulphonamide*, m.p. 88°. H. W.

Manufacture of sulphonyl chlorides.—See B., 1942, II, 307.

Direct introduction of sulpho-groups in aliphatic compounds by means of chlorine–sulphur dioxide mixtures and of sulphuryl chloride. J. H. Helberger (*Angew. Chem.*, 1942, **55**, 172—174).—A review.

Absorption spectra of compounds containing sulpho-groups.—See A., 1942, I, 385.

Dimethyl-β-acetoxyethylsulphonium chloride, the sulphur analogue of acetylcholine chloride. V. Prelog, S. Junäsz, A. Režek, and P. Stern (*Helv. Chim. Acta*, 1942, **25**, 907—911).—SMe·$[CH_2]_2$·OH is converted by MeI followed by AgCl into the very hygroscopic dimethyl-β-hydroxyethylsulphonium chloride (analysed as the *platinichloride*, m.p. 191—192°), which with AcCl in $CHCl_3$ at room temp. yields dimethyl-β-acetoxyethylsulphonium chloride (**I**) (characterised as the *reineckate*, m.p. 147—149°). Pharmacologically and in its behaviour towards choline-esterase (**I**) closely resembles acetylcholine. The pharmacological activity is depressed in the ratio ~10 : 1 and the acceleration of the hydrolytic fission by choline-esterase is less. H. W.

Producing conjugation in unconjugated polyenes.—See B., 1942, II, 306.

Preparation of esters from acid chlorides and alcohols in presence of metals. A. Spassow (*Ber.*, 1942, **75**, [*B*], 780—784).—The influence of Na, Ca, Mg, Al, and Zn has been studied on the reaction between $Bu^{\beta}OH$ *sec.*-BuOH, $Bu^{\gamma}OH$, and CMe_2Et·OH and AcCl, $Pr^{\alpha}COCl$, and CH_2Ph·COCl. In the case of primary alcohols the metals have little effect with the exception of Na, which depresses the yield by ~23%. Zn is favourable for the esterification of *sec.* alcohols but very unsuitable for that of *tert.* alcohols. In presence of Al the yield of ester is usually somewhat < that obtained by direct acylation. Ca and Mg alone cause increase in the yields of esters from all *sec.* and *tert.* alcohols, Ca being less active than Mg, which is particularly suitable for *tert.* alcohols. The diminution of ester yield in the presence of Na is ascribed to ester condensation and in that of Zn to production of olefines or chlorination. Such reactions do not appear to occur with Ca and particularly with Mg. H. W.

Vapour-phase photo-decomposition of methyl formate.—See A., 1942, I, 404.

[Photo-sensitivity of] acyclic acids.—See A., 1942, I, 404.

Oxidation of ascorbic acid in presence of copper.—See A., 1942, III, 763.

Alkyl–oxygen fission in carboxylic esters. I. Esters of αγ-dimethylallyl alcohol and other substituted allyl alcohols. M. P. Balfe, H. W. J. Hills, J. Kenyon, H. Phillips, and B. C. Platt (*J.C.S.*, 1942, 556—559).—The optical activity of the products of reaction of the (+)-H phthalate (**I**) of CHMe:CH·CHMe·OH with HCO_2H, AcOH, MeOH, BuOH, CH_2Ph·OH, and PhOH, and of the (+)-benzoate with HCO_2H, AcOH, MeOH, and BuOH, has been investigated. The products are extensively racemised. When the reaction is stopped before completion, the unchanged ester is in many cases partly racemised. Both results indicate alkyl–O fission. (−)-CHMe:CH·CHMe·OH in presence of conc. H_2SO_4 at room temp. yields considerably racemised $(CHMe:CH·CHMe)_2O$. At 31°, (**I**) is stable in MeOH, but in $MeNO_2$ during 61 days is 20% decomposed [giving *o*-$C_6H_4(CO_2H)_2$], the remainder being 90% racemised. *Phαγ-dimethylallyl ether* has b.p. 97°/13 mm. A. Li.

Manufacture of trifluoroacetyl halide.—See B., 1942, II, 308.

Mixed anhydrides of formic and acrylic acid and α-substituted acrylic acids.—See B., 1942, II, 309.

Co-polymerisation of alkyl acrylates and maleates. Kinetic studies of co-polymerisation. C. S. Marvel and R. L. Frank (*J. Amer. Chem. Soc.*, 1942, **64**, 1675—1678).—The rate of co-polymerisation of *l*-monomenthyl maleate (**I**), m.p. 86—87°, $[\alpha]_D^{28}$ −74·3° in EtOH, and CH_2:CH·CO_2Et (**II**) in presence of >5% of Bz_2O_2 is zero order with respect to (**I**) (independent of concn.) and independent of the [(**II**)], but ∝ $[Bz_2O_2]$. When 2 mols. of (**I**) co-polymerise with 1 mol. of (**II**), a zero-order reaction occurs until the (**I**) is used up and a slower reaction then follows. As judged by α, (**I**) and Bz_2O_2 undergo a first-order reaction, which does not occur when (**II**) is present. The polymeride always contains <50 mol.-% of (**I**). *l-Menthyl β-chloropropionate* (prep. by the chloride in C_6H_6), b.p. 105—107°/4 mm., $[\alpha]_D^{26}$ +25·8° (homogeneous), in quinoline at 170—180° gives *l-menthyl acrylate* (**III**), b.p. 78—80°/5 mm., $[\alpha]_D^{28}$ −80·2° in dioxan. Polymerisation of (**III**) is a first-order reaction. The kinetics of co-polymerisation of (**III**) and $Et_2C_2O_4$ are obscure. R. S. C.

Esters of dihalogenopropionic acid.—See B., 1942, II, 309.

Potassium oxalatostannate.—See A., 1942, I, 405.

Complex dioxalothiometastannates.—See A., 1942, I, 405.

Solid $\Delta^{\iota\lambda}$-*n*-octadeeadienoic acid. Conjugated linoleic acid melting at 57°. J. D. von Mikusch (*J. Amer. Chem. Soc.*, 1942, **64**, 1580—1582).—Fatty acids from dehydrated castor oil, when heated with aq. NaOH, yield >20% of a $\Delta^{\iota\lambda}$-n-*octadecadienoic acid* (**I**), m.p. 56·3—57·7° (corr.) [insol. Pb salt, m.p. ~115°; *Me* ester (**II**), m.p. 25°, b.p. 207—208°/9 mm. (diene val. 87); tetrabromides, m.p. 149·5—150·5° and 104—105° (corr.); exaltation of *n* +3·43]. $KMnO_4$ oxidises (**I**) in alkali to di-, liquid, and tetra-hydroxystearic, m.p. 187—188·5° (corr.), and sebacic acid, or (**II**) in $COMe_2$ to *n*-octoic and sebacic acid. (**I**) is not formed from the acids of soya-bean or walnut oil and is thus derived from an isomeride of the usual $\Delta^{\theta\lambda}$-linoleic acid. R. S. C.

Autoxidation of oxygen-active acids. IV. Refractometric analysis of addition of oxygen to the methyl esters. W. Treibs (*Ber.*, 1942, **75**, [*B*], 925—933; cf. A., 1942, II, 346).—Refractometric analysis like the volumetric, gravimetric, and viscosimetric observation of the autoxidation phenomena shows that there is a fundamental difference between the action of mol. O_2 on Me elæostearate (**I**) and on the Me esters of linoleic (**II**), linolenic (**III**), and the hexaenoic acid (**IV**). After the monoperoxide stage is reached with (**I**) there is a marked saturation of the double linking whereas with (**II**), (**III**), and (**IV**) the degree of saturation is scarcely or not lessened in a refractometrically appreciable degree. The simplest explanation of this effect in (**II**), (**III**), and (**IV**) lies in the assumption that the activated O_2 mol. has become interposed in a CH_2 group between two double linkings. Possibly the initial change is the unsymmetrical, enol-like intrusion of O_2 into a double linking and subsequent passage into the ethylene oxide arrangement under the influence of polarising agencies (*e.g.*, in the determination of I val.) thus: ·CH:CH·CH_2·CH:CH· → ·CH:CH·CH_2·CH·C(O_2H)· → CH:CH·CH_2·CH_{OO}CH·. H. W.

Ambrettolide and its isomerides. I. Synthesis of ω-hydroxy-Δ$^{\varepsilon}$-hexadecenoic acid and its lactone. C. Collaud (*Helv. Chim. Acta*, 1942, **25**, 965—977).—Gradual addition of *cyclo*hexanone in Et_2O to Mg Δ$^{\kappa}$-undecenyl chloride in the same solvent gives 1-Δ$^{\kappa}$-*undecenyl*-cyclo*hexanol*, b.p. 147—150°/2 mm. (3 : 5-*dinitrobenzoate*, m.p. 56°), ozonised in 95% AcOH and then converted by Zn dust into (not isolated) ι-aldehydononyl*cyclo*hexanol (*semicarbazone*, m.p. 94—95°), which is reduced (H_2 at 100°/20 atm.; Raney Ni–EtOH) to *κ-hydroxydecyl*cyclo*hexanol*, m.p. 64—65°. This is dehydrated by rapid distillation under reduced pressure in presence of $KHSO_4$ to 1-*κ-hydroxydecyl*-Δ^1-cyclo*hexene*, b.p. 138—140°/0·1 mm. (*acetate*, b.p. 136—138°/0·05 mm.; *phenylurethane*, m.p. 68—69°), which is converted into the corresponding *ozonide*, m.p. 98—100°, which is reduced by Zn dust and then oxidised by Ag_2O to ε-*keto-ω-hydroxyhexadecoic acid*, m.p. 90—91° (*semicarbazone*, m.p. 147°). This is hydrogenated (Raney Ni) in feebly alkaline solution to *εω-dihydroxyhexadecoic acid*, m.p. 111—112° (*diformate*, m.p. 72·5°), which does does not appear to yield an estolide. It is transformed by *o*-$C_6H_4(CO)_2O$ at 150° and then at 280° into a mixture rich in unsaturated acids which are separated from one another with great difficulty; C_6H_6 allows the separation of 70% of cryst. slightly sol. acids, one of which (**I**) has m.p. 71—72°, and ~30% of acids which are freely sol. and liquid at room temp. The Na salts of the crude acids are mixed with glycerol; after part of this solvent has been distilled the mixture is cooled to 150°, treated with CH_2Cl·CH(OH)·CH_2·OH (**II**), and kept at 150° for 1 hr., after which excess of (**II**) and a further quantity of glycerol are distilled under diminished pressure. After cooling, NaOMe in MeOH is added; excess of MeOH is distilled followed by the glycerol, which carries with it the lactones. These are not separable from one another by fractional distillation and are hydrolysed to a mixture of *iso*ambrettolic acids from which (**I**) is isolated by reason of its sparing solubility in C_6H_6. It is ozonised and then reduced to aldehydes, which on oxidation afford adipic and ι-hydroxydecoic acid. (**I**) is therefore *ω-hydroxy-Δ$^{\varepsilon}$-hexadecenoic acid*. It is oxidised by $KMnO_4$ to *εζo-trihydroxydecoic acid*, m.p. 100—101° (p-*phenylphenacyl* ester,

m.p. 94—95°), and converted by the method described above into its *lactone* (Δ^{ϵ}-iso*ambrettolide*), b.p. 153°/2·5 mm., hydrolysed to (**I**). H. W.

Carboxylation. III. Peroxide-catalysed interaction of oxalyl chloride with the side-chains of aralkyl hydrocarbons. Relative reactivity of free radicals. M. S. Kharasch, S. S. Kane, and H. C. Brown (*J. Amer. Chem. Soc.*, 1942, **64**, 1621—1624; cf. A., 1942, II, 215).—Low reactivity of $(COCl)_2$ with aryl and aralkyl hydrocarbons is due partly to absorption of the active light and partly to low reactivity of the free radical with $(COCl)_2$. Thus, photochemical carboxylation of PhMe, *m*-xylene, *s*-$C_6H_3Me_3$, *p*-C_6H_4MeCl, tetrahydronaphthalene, and 2-$C_{10}H_7Me$ by $(COCl)_2$ is impossible, and that of *cyclo*hexane is largely suppressed by presence of C_6H_6 but not by that of CCl_4, $CHCl_3$, or CH_2Cl_2. Secondly, presence of Bz_2O_2 leads to >10% of acid from *m*-xylene, *s*-$C_6H_3Me_3$, or *p*-C_6H_4MeCl. The results are paralleled by interaction of free radicals from $(AlkCO)_2$, $(ArCO)_2$, and $(CH_2Ar{\cdot}CO)_2$ with CCl_4; thus, Ac_2, $(Pr^{\alpha}CO)_2$, and $(Pr^{\beta}CO)_2$ in CCl_4 give 10—20% of MeCl, $Pr^{\alpha}Cl$, and $Pr^{\beta}Cl$, respectively, but $(Bu^{\gamma}CO)_2$ and $(CH_2Ph{\cdot}CO)_2$ give no chloride. These and other results differentiate Ph, Me, Pr^{α}, and Pr^{β} as more reactive radicals than CH_2Ph, Bu^{γ}, and CPh_3. Correlation between this and the electronegativity series is probably not fortuitous. R. S. C.

Dehydration of maleic acid.—See B., 1942, II, 309.

Preparation of dicarboxylic acids connected with the synthesis of civetone. II. Preparation of *cis*- and *trans*-Δ^{θ}-hexadecene-$\alpha\pi$-dicarboxylic acid. L. Ruzicka, P. A. Plattner, and W. Widmer (*Helv. Chim. Acta*, 1942, **25**, 1086—1098).—Δ^{θ}-Undecinoic acid (**I**), m.p. 59·5—61·5°, is converted by boiling 2% HCl–MeOH into its *Me* ester (**II**), b.p. 93—94°/1 mm., accompanied by a mixture of Me ϑ- and ι-ketoundecoate, the latter of which affords a *semicarbazone*, m.p. 121—122°. Acyloin condensation of (**II**) leads to *λμ-diketo-*$\Delta^{\beta\phi}$*-docosadi-inine*, m.p. 60·5—61·5°, and *λ-keto-μ-hydroxy-*$\Delta^{\beta\phi}$*-docosadi-inine*, m.p. 50—51°, which is re-converted by $Pb(OAc)_4$ in AcOH into (**I**). Reduction (Meerwein–Ponndorf) of the mixture gives the stereoisomeric α- (**III**), m.p. 86—87°, and β- (**IV**), m.p. 118—119°, *-λμ-dihydroxy-*$\Delta^{\beta\phi}$*-docosadi-inine* (corresponding *diacetates*). (**IV**) is converted by the successive action of $Pb(OAc)_4$–AcOH and Ag_2O into (**I**). Hydrogenation (Raney Ni in EtOH) of (**III**) and (**IV**) yields respectively α-, m.p. 82·5—83·5°, and β-, m.p. 128—129°, *-λμ*-dihydroxydocosane. Ozonisation of the glycol diacetates and oxidation of the products with $KMnO_4$ leads to α- (**V**), softens at 118°, m.p. 121—122·5° (*Me_2* ester softens at 67°, m.p. 69—72°), and β- (**VI**), m.p. 157—159° (*Me_2* ester, m.p. 100—102°), *-θι-dihydroxyhexadecoic acid.* (**V**) and HBr–AcOH at room temp. afford the *α-Br_2*-acid [isolated as the *Me_2* ester (**VII**), m.p. 44·5—45·5°], whilst (**VI**) yields the *β-Br_2*-acid, softens at 65°, m.p. 73—76° [*Me_2* ester (**VIII**)]. Debromination of (**VII**) gives *Me_2* α-Δ^{θ}*-hexadecene-*$\alpha\pi$*-dicarboxylate*, m.p. 32—33·5° (*acid*, softens at 97°, m.p. 98·5—99·5°), whereas debromination and hydrolysis of (**VIII**) yields β-Δ^{θ}*-hexadecene-*$\alpha\pi$*-dicarboxylic acid*, softens at 68°, m.p. 70—71·5° [*Me_2* ester (**IX**)]. Azelaic acid is obtained by the ozonisation of either acid. (**IX**) is hydrogenated (Raney Ni in MeOH) to Me hexadecane-$\alpha\pi$-dicarboxylate, m.p. 59·5—60·5° (acid, softens at 121°, m.p. 124—125°). β-Δ^{θ}-Hexadecene-$\alpha\pi$-dinitrile, from the β-acid by the action of $SOCl_2$, then NH_3 followed by $SOCl_2$, has b.p. ~210°/0·03 mm. H. W.

Benziminazole rule for determination of configuration of aldonic acids and related compounds. N. K. Richtmyer and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 1612—1613).—When the OH at $C_{(\alpha)}$ of an aldonic acid is on the right in the conventional projection formula, [α] of the derived benziminazole is positive (if on the left, negative). If the configurations at $C_{(\alpha)}$, $C_{(\beta)}$, and $C_{(\gamma)}$ are +++ or ++−, [*M*] is low (>7350); if +−− or −++, [*M*] is high (11,750—14,750); if +−+ or −+−, [*M*] cannot be predicted. The following new $[\alpha]_D^{20}$ are recorded, vals. being for solutions in 5% citric acid and N-HCl, respectively: 2-*D-arabo-*, −49·4°, −49·7°, 2-*L-arabo-*, +49·7°, +49·8°, and 2-D-ribo-*tetrahydroxy*-n-*butyl-* [m.p. ~190° (decomp.)], −21·6°, —, 2-D-glucomethylo- [m.p. ~190° (decomp.)], +7·6°, —, 2-*D-galacto-*, +44·5°, +45·1°, 2-L-galacto- [m.p. ~250° (decomp.)], −44·1°, −45·0°, and 2-*D*-glucopentahydroxy-*n*-amyl-, +9·5°, +8·7°, and 2-D-gluco-L-galacto*heptahydroxy*-n-*heptyl-* [m.p. 246—247° (decomp.)], —, −44·7°, *-benziminazole.* R. S. C.

Catalysis of the thermal decomposition of acetaldehyde by hydrogen sulphide.—See A., 1942, I, 402.

Abnormal Grignard reactions. XIV, XV. Sterically hindered aliphatic carbonyl compounds. IV. Methyl triethylcarbinyl ketone and its bromomagnesium enolate. F. C. Whitmore and C. E. Lewis. **V. Enolisation. I.** F. C. Whitmore and L. B. Block (*J. Amer. Chem. Soc.*, 1942, **64**, 1618—1619, 1619—1621; cf. A., 1942, II, 348).—XIV. $CEt_3{\cdot}COCl$ and MgMeBr in Et_2O give 0·5 CH_4; successive products are $COMe{\cdot}CEt_3$ (**I**) (34%), b.p. 90°/60 mm. (oxime, m.p. 97—101°; 2 : 4-dinitrophenylhydrazone, m.p. 93—94·5°), $CEt_3{\cdot}CO{\cdot}CH_2{\cdot}MgBr$, and $CH_2(CO{\cdot}CEt_3)_2$ (32%), b.p. 135—136°/8 mm. (Cu derivative, m.p. 143—144°). With MgMeBr, (**I**) shows 94% enolisation and no addition. With MgEtBr and then CH_3O and CO_2 it gives *γ-keto-*δδ*-diethyl*-n-*hexanol* (34%), b.p. 86°/2 mm. (α-naphthylurethane, m.p. 120—122°), and *β-keto-γγ-diethyl*-n-*hexoic acid* (21%), m.p. 63—65° [gives CO_2 and (**I**)], respectively.

XV. Steric hindrance (Et ≫ Me) may inhibit both enolisation and addition in the Grignard machine. The following are % enolisation and addition, respectively, with MgMeCl: $COMePr^{\beta}$, $COEtPr^{\beta}$ 0, 100, $COMeBu^{\gamma}$ 5, 86, $COEtBu^{\gamma}$ 9, 86, $COPr^{\beta}Bu^{\gamma}$ 0, 49, $COMe{\cdot}CHMeBu^{\gamma}$ 48, 47, $COEt{\cdot}CHMeBu^{\gamma}$ 62, 33, $COMe{\cdot}CHMeEt$ 32, —, $COPr^{\alpha}{\cdot}CHMeEt$ 53, 40, $COBu^{\gamma}{\cdot}CHEt_2$ 5, 19, and $CHMe(COBu^{\gamma})_2$ 27/2, 129/2. R. S. C.

Detection and inhibition of free radical chain reactions.—See A., 1942, I, 402.

[Materials for] heterocyclic syntheses. I. Substituted β-diketones. L. Panizzi (*Gazzetta*, 1941, **71**, 216—228).—$CHCl_2{\cdot}CO_2Et$ and $COMe_2$ (**I**) with Na in Et_2O, followed by dil. H_2SO_4, give *αα-dichloroacetylacetone*, b.p. 83°/7—8 mm., which is isolated through its *Cu* salt, m.p. 197—198° (decomp.), and is hydrolysed by NaOH to (**I**) and $CHCl_2{\cdot}CO_2H$. $COMe{\cdot}C(:N{\cdot}OEt){\cdot}CO_2Et$ (**II**) (A., 1938, II, 311) with $Et_2C_2O_4$ and NaOEt in Et_2O gives a product which in EtOH with $Cu(OAc)_2$ gives the *Cu* salt, m.p. (+H_2O) 122—124°, (anhyd. m.p. 163—164°), of *Et α-ethoxyimino-ββ-diketoadipate*, an oil, which with boiling 8% NaOH gives $H_2C_2O_4$, HCN, AcOH, and CO_2. With HCO_2Me and NaOEt or Na in Et_2O, (**II**) gives, by an obscure condensation, HCN and *Et α-ethoxyimino-ββδ-diketohexoate*, b.p. 135—136°/2—4 mm. (*Cu* salt, m.p. 97—98°), decomposed by KOH into HCN and (**I**). $COMe{\cdot}CMe{:}N{\cdot}OEt$ (**III**), which with $Et_2C_2O_4$–Na–Et_2O gives $CO_2Et{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CMe{:}N{\cdot}OEt$ (*Cu* salt), with HCO_2Et and Na–Et_2O, followed by aq. $Cu(OAc)_2$, gives the *Cu* salt, decomp. 160°, of α-methoxyimino-*n*-propionylacetaldehyde (not isolated). With EtOAc and Na–Et_2O, (**III**) gives *ε-methoxyimino-ββδ-diketohexane*, b.p. 85—86°/5—7 mm., of which the *Cu* salt, decomp. >170°, with KOH gives (**I**). E. W. W.

Transformation of hydroxymethylene ketones into benzene derivatives.—See A., 1942, I, 401.

Preparation of ketoximes.—See B., 1942, II, 310.

Macromolecular compounds. Polyamines and polyethyleneimines.—See A., 1942, I, 363.

Production of aliphatic amino-alcohols.—See B., 1942, II, 310.

Synthesis of β-alkylaminoethanols from ethanolamine. A. C. Cope and (Miss) E. M. Hancock (*J. Amer. Chem. Soc.*, 1942, **64**, 1503—1506).—Hydrogenation of $OH{\cdot}[CH_2]_2{\cdot}NH_2$ + aldehydes or ketones gives good yields of alkylaminoethyl alcohols. Sometimes oxazolidines can be isolated as intermediates and occasionally alkylideneamino-alcohols; structures of these are determined by the b.p., ease of hydrolysis, and *n*, which indicate occasionally ring–chain tautomerism. PtO_2 in EtOH at room temp., sometimes 50—60°, is used; Pd–C at 60° is less effective; AcOH may be used. Raney Ni or Cu chromite in EtOH with or without a solvent is also effective. The following are described. *β-iso*Propyl-, b.p. 76—77°/15 mm. (picrate, m.p. 127—128·5°), β-sec.-*butyl-*, b.p. 88—88·5°/17 mm. (*picrate*, m.p. 98—100°), β-sec.-*amyl-*, b.p. 98—99°/15 mm. (*picrate*, m.p. 90—92), *β-α′-ethyl*-n-*propyl-*, b.p. 85—85·5°/8 mm. (*picrate*, m.p. 98—99°), *β-α′-methyl*isoamyl-, b.p. 102—102·5°/13 mm. (*picrate*, m.p. 105—106°), *β-α′-methyl*-n-*hexyl-*, b.p. 115—116°/10 mm. (*picrate*, m.p. 70—71°), *β-α′*-n-*propyl*-n-*butyl-*, b.p. 104—105°/8 mm. (*picrate*, m.p. 112—113°), *β-α′-methyl*-n-*heptyl-*, b.p. 130—130·5°/12 mm. (*picrate*, m.p. 67—69°), *β-α′-methyl*-n-*octyl-*, b.p. 138—139°/10 mm. (*picrate*, m.p. 73—74°), *β-α′*-n-*butyl*-n-*amyl-*, b.p. 130·5—131°/9 mm. (*picrate*, m.p. 112—113°), *β-α′*-iso*butyl*iso*amyl-*, b.p. 113—114°/7 mm. (*picrate*, m.p. 150—151°), *β-α′-methyl*-n-*octyl-*, b.p. 149—150°/9 mm. (*picrate*, m.p. 66—68°), *β-cyclo*hexyl-, m.p. 40—41°, b.p. 122—123·5°/13 mm. (*picrate*, m.p. 128—129°), *β*-2-*methyl*cyclo*hexyl-*, b.p. 123·5—124°/13 mm. (*picrate*, m.p. 120—122°), *β*-4-*methyl*cyclo*hexyl-*, b.p. 129·5—130°/14 mm. (*picrate*, m.p. 116—117°), *β*-2 : 2 : 6-*trimethyl*cyclo*hexyl-*, b.p. 123—123·5°/7 mm. (*picrate*, m.p. 142—142·5°), β-l-*menthyl-*, b.p. 134·5—136°/7 mm. (*picrate*, m.p. 118—120°), *β-α′-phenylethyl-*, b.p. 139—140°/9 mm. (*picrate*, m.p. 139—140°), *β-n-*, b.p. 91—92°/11 mm. [picrate, m.p. 86—88° (lit. 98°); picrolonate, m.p. 211—213° (lit. 218°)], and *β-iso*-butyl-, b.p. 89—90°/16 mm., *β-n*-amyl-, b.p. 114—115°/19 mm. (*picrate*, m.p. 64—65°), β-n-*heptyl-*, m.p. 30—32°, b.p. 120—121°/7 mm. (*picrate*, m.p. 69—70°), and *β-β′-ethyl*-n-*hexyl-*, b.p. 119—120°/8 mm. (*picrate*, m.p. 104—106°), *-aminoethyl alcohol*; 2 : 2-*pentamethylene-*, b.p. 89—90°/16 mm., 2-*methyl*-2-n-*amyl-*, b.p. 88—90°/7 mm., and 2-*methyl*-2-n-*propyl-oxazolidine*, b.p. 62—62·5°/16 mm. (equilibrates with $CMePr^{\alpha}{:}N{\cdot}[CH_2]_2{\cdot}OH$ when kept); α-iso*butyl*iso*amylideneaminoethyl alcohol*, b.p. 110—111°/8 mm. R. S. C.

Selenium tetracysteine. J. A. Stekol (*J. Amer. Chem. Soc.*, 1942, **64**, 1742).—Cysteine hydrochloride and aq. Na_2SeO_3 gives *Se tetracysteine*, $Se(S{\cdot}C_3H_6O_2N)_4$, darkens at 164—165°, decomp. 195—196°, which in warm, dil. acid or cold, dil. alkali decomposes, yielding Se. R. S. C.

Degradation of *d*-amino-acids by *d*-amino-acid oxidase. P. Karrer, H. Koenig, and R. Appenzeller (*Helv. Chim. Acta*, 1942, **25**,

911—918; cf. Karrer and Frank, A., 1940, III, 931).—Repetition of previous work in consequence of the criticisms of Klein and Handler (A., 1941, III, 702) and Holtz and Bächsel (A., 1942, III, 846) shows that *dl*-aspartic acid (**I**), *dl*-histidine (**II**), and *dl*-dihydroxyphenylalanine scarcely absorb O_2 under the influence of the "reconstructed" enzyme whereas serine is appreciably dehydrogenated. (**I**) and (**II**) are dehydrogenated by crude extracts of kidney powder but less rapidly than is alanine (**III**). Mixtures of (**I**) or (**II**) with (**III**) are dehydrogenated as rapidly as is (**III**) alone. Dehydrogenation of (**I**) or (**III**) by crude amino-acid oxidase is not accelerated by the addition of lactoflavin-adenine dinucleotide or Warburg's protein solution *B*. H. W.

Mononitrile, m.p. 180—182°, of αα′-iminodipropionic acid.—See A., 1942, III, 847.

Salts and complex compounds of nitrilotriacetic acid.—See A., 1942, I, 405.

Dipole moment and structure of carbamide and thiocarbamide.—See A., 1942, I, 388.

II.—SUGARS AND GLUCOSIDES.

Azoyl derivatives of sugars. Separation by chromatographic adsorption. G. H. Coleman, A. G. Farnham, and A. Miller (*J. Amer. Chem. Soc.*, 1942, **64**, 1501—1502).—*p*-$COCl{\cdot}C_6H_4{\cdot}N_2Ph$ and the appropriate sugar in C_5H_5N at 0° (8—20 days) give α-, m.p. 234—236°, $[\alpha]_D^{25}$ +282°, $[\alpha]_{6438}^{25}$ +226° (all [α] are in $CHCl_3$), and β-D-*glucose*, m.p. 204—206°, $[\alpha]_D^{25}$ +111°, $[\alpha]_{6438}^{25}$ +86°, and α-D-*galactose penta-azobenzene-4-carboxylate*, m.p. 224—226°, $[\alpha]_D^{25}$ +504°, $[\alpha]_{6438}^{25}$ +399°, impure *D*-xylose, m.p. 146—148°, $[\alpha]_D^{25}$ +285°, $[\alpha]_{6438}^{25}$ +225°, and β-D-*fructose tetra-azobenzene-4-carboxylate*, m.p. 128—130°, $[\alpha]_D^{25}$ −511°, $[\alpha]_{6438}^{25}$ −394°, α-lactose, m.p. 218—220°, $[\alpha]_D^{25}$ +355°, $[\alpha]_{6438}^{25}$ +274°, *trehalose*, m.p. 123—125°, $[\alpha]_D^{25}$ +276°, $[\alpha]_{6438}^{25}$ +217°, and *sucrose octa-azobenzene-4-carboxylate*, m.p. 125—126°, $[\alpha]_D^{25}$ +43°, $[\alpha]_{6438}^{25}$ +35°, *β-cellobiose*, m.p. 206—208°, $[\alpha]_{6438}^{25}$ +101°, *β-gentiobiose*, m.p. 159—161°, $[\alpha]_{6438}^{25}$ +28°, and *β-maltose* (? *hepta-azobenzene-4-carboxylate*, m.p. 253—255° (242—244°), $[\alpha]_D^{25}$ −30°, $[\alpha]_{6438}^{25}$ −22°, and melezitose (poly)azobenzene-4-carboxylate, m.p. 135—137°, $[\alpha]_D^{25}$ +110°, $[\alpha]_{6438}^{25}$ +81°. Numerous but not all pairs of esters are separated by chromatography on SiO_2 or Magnesol + Dicalcite. R. S. C.

Action of diazomethane on acyclic sugar derivatives. II. W. L. Wolfrom, S. W. Waisbrot, and R. L. Brown (*J. Amer. Chem. Soc.*, 1942, **64**, 1701—1704).—Partly a detailed account of work already reported (A., 1942, II, 122; cf. *ibid.*, 87). The structure of α-deoxy-*d*-glucoheptonolactone is discussed in view of absence of mutarotation of it and its tetra-acetate. *d*-Arabonic acid tetra-acetate with warm $SOCl_2$–C_6H_6 and then CH_2N_2–Et_2O at 0° gives 1-*diazo*-1-*deoxy*keto-d-*fructose tetra-acetate*, m.p. 93—94°, $[\alpha]_D^{23}$ −11° in $CHCl_3$, converted by HCl– and HBr–Et_2O into 1-*chloro*-, m.p. 77·5—78°, $[\alpha]_D^{22}$ +68° in $CHCl_3$, and 1-*bromo*keto-d-*fructose tetra-acetate*, m.p. 68°, $[\alpha]_D^{26}$ +62·5° in $CHCl_3$, respectively. R. S. C.

***d*-Allulose and some methylated derivatives.** F. W. Zerban and L. Sattler (*J. Amer. Chem. Soc.*, 1942, **64**, 1740—1741).—Commercial distillery residues yield, by way of the $(CMe_2{:})_2$ derivative, *d*-allulose [*d*-psicose], a syrup, $[\alpha]_D^{20}$ +2·9° in H_2O, or by methylation methyl-1 : 3 : 4 : 6-tetramethyl-*d*-alluloside, b.p. 105—140° (bath)/0·00004 mm., $[\alpha]_D^{20}$ (after equilibration by HCl–MeOH at 100°) +36°. R. S. C.

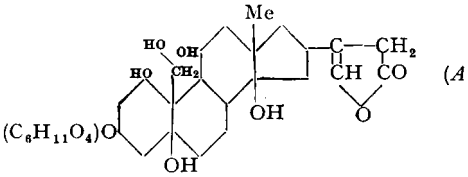
***L*-Glucoheptulose.** W. D. Maclay, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 1606—1609).—*Acetobacter suboxydans* converts *D*-gluco-*D*-guloheptitol in aq. KH_2PO_4–yeast extract–glucose–air at 30° into *L*-glucoheptulose (**I**) (88%), m.p. 172—173°, [α] −67·8° in H_2O (*phenylosazone*, m.p. 181—182°, $[\alpha]_D^{20}$ +6·0° → −35·3° in 96 hr. in 2 : 3 C_5H_5N–EtOH; *D*-isomeride, $[\alpha]_D^{20}$ −5·6° → +34·9°; *racemate*, m.p. 176—177°, *a* 0) (cf. Bertrand *et al.*, A., 1928, 620; Austin, A., 1930, 894), reduced by H_2–Raney Ni in H_2O at 100°/167 atm. to *L*-gluco-*L*-gulo- (hepta-acetate, m.p. 118—119°, *a* 0) and L-*gluco*-L-*ido-heptitol* (**II**), m.p. 129—130°, $[\alpha]_D^{20}$ −0·8° in H_2O (hepta-acetate, an oil; *heptabenzoate*, m.p. 181—182°, $[\alpha]_D^{20}$ −25·3° in $CHCl_3$) (proof of structure), separated by way of the acetates. (**I**) and its *D*-form give a mixture, m.p. 150—152°, $[\alpha]_D$ ±0°, but (**II**) and its *D*-form (prep. from *D*-gluco-*D*-idoheptose by H_2–Raney Ni), m.p. 129—130°, $[\alpha]_D^{20}$ +0·7° in H_2O (heptabenzoate, $[\alpha]_D^{20}$ +25·1° in $CHCl_3$), give a *racemate*, m.p. 114—115°, *a* 0 (dl-*heptabenzoate*, m.p. 193—194°, *a* 0, similarly prepared). Crystallo-optical data of the products are recorded. M.p. are corr. R. S. C.

Oxidative degradation of *L*-glucoheptulose. N. K. Richtmyer and C. S. Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 1609—1611).—*L*-Glucoheptulose with O_2 in N-KOH at 20—25° gives *L*-arabonic (31%) [K salt, m.p. ~220° (decomp.), $[\alpha]_D^{20}$ −5·0±0·1° in H_2O], *L*-gluconic (**I**), *L*-erythronic (**II**), and OH-C_{2-3}-acids. (**I**) is identified as brucine, m.p. 180° (gas), $[\alpha]_D^{20}$ −28·6° in H_2O, and *K* salt, m.p. ~185° (decomp.), $[\alpha]_D^{20}$ −11·3±0·2° in H_2O, and benziminazole derivative, and (**II**) as brucine salt, m.p. ~210° (decomp.), $[\alpha]_D^{21}$ −31·6° in H_2O, lactone, m.p. 102—103°, $[\alpha]_D^{20}$ +73·0° in H_2O, and 2-D-erythro*trihydroxypropylbenziminazole*, m.p. 177—178°, $[\alpha]_D^{20}$ +9·0±0·2° in 5% citric acid (*L*-form, $[\alpha]_D^{20}$ −8·3±0·2°). Isolation of (**I**) completes the conversion of *D*- into *L*-glucose. R. S. C.

Synthesis of the glucoside of resacetophenone. F. Mauthner (*J. pr. Chem.*, 1942, [ii], **160**, 33—37).—Resacetophenone (improved prep.) and acetobromoglucose in quinoline–Ag_2O give *glucoresacetophenone tetra-acetate*, m.p. 131—132°, hydrolysed by aq. $Ba(OH)_2$ at room temp. to *glucoresacetophenone*, m.p. 201—202°. Pæonol [2 : 4 : 1-OH·C_6H_3(OMe)·COMe] similarly gives *tetra-acetylglucopæonol*, m.p. 144—145°, and thence *glucopæonol*, m.p. 82—83°. A. T. P.

Uterine principle [glucoside] from *Viburnum prunifolium*.—See A., 1942, III, 842.

***g*-Strophanthin (ouabain) and *g*-strophanthidin.** C. Mannich and G. Siewert (*Ber.*, 1942, **75**, [*B*], 737—750).—Crystallisation of *g*-strophanthin (**I**) from dioxan containing a little H_2O gives a *trihydrate* which is dehydrated to (**I**), m.p. 241° instead of 187—188° as is customary. Anhyd. (**I**), $CuSO_4$, and $COMe_2$ yield iso*propylidene-g-strophanthin*, m.p. (indef.) 145—160°, also obtained by use of HCl–$COMe_2$. Prolonged contact with the last reagent causes the conversion of (**I**) into iso*propylidene-g-strophanthin* (**II**), m.p. 200—235° (the properties of which vary somewhat in different specimens as its complete insolubility prevents purification), with a smaller proportion of *anhydro-g-strophanthidin* (**III**), m.p. 303—305°, which has only slight physiological activity and gives a positive Legal test. Fission can be effected in other ketonic solvents, iso*butylidene*-, m.p. (indef.) 210—230°, and cyclo*hexylidene*-, m.p. 248—252°, *-g-strophanthidin* being obtained in presence of COMeEt and *cyclo*hexanone respectively. Other acids such as *p*-$C_6H_4Me{\cdot}SO_3H$ are used with less advantage. The fission is not a hydrolysis since it occurs in absence of H_2O and appears to be due to HCl mols. Some Cl is found in org. combination. (**III**) is converted by 0·6% H_2SO_4 at room temp. or by boiling 50% EtOH into *g-strophanthidin* (**IV**), $C_{23}H_{34}O_8$, m.p. (anhyd.) 255—256° (+1H_2O, m.p. 235—238°) $[\alpha]_D^{17}$ +11·32° in H_2O, which gives the Legal reaction and is titrated as a lactone. With dioxan and HCl it affords the *compound*, $C_{23}H_{34}O_8{,}C_4H_8O_2{,}HCl$, m.p. 133—135°. (**IV**) is hydrogenated (PtO_2 in AcOH) to *dihydro-g-strophanthidin* (**V**) (+1MeOH), m.p. 261°, which does not show the Legal reaction. (**IV**) contains 6 OH of which 4 are readily acetylated since Ac_2O and C_5H_5N transform (**IV**) and (**V**) into *tetra-acetates*, anhyd. and +3H_2O, m.p. 282—285° and m.p. 264—265° respectively. The remaining 2 OH are *tert.* Attempted prep. of an *iso*genin by treatment with alkali hydroxides gives only an amorphous product which does not give the Legal reaction. Oxidation (Criegee) of (**IV**) and (**V**) leads to so small a consumption of $Pb(OAc)_4$ that a 1 : 2-glycol cannot be present; (**II**) therefore contains the CMe_2: united to 2 O in the 1 : 3-position. The action of (**IV**) on the heart is marked but considerably less powerful than that of (**I**). Mild acetylation of (**I**) leads to a *hexa-acetate*, m.p. 288—290°, in which 3 Ac are united to the rhamnose residue and 3 to the genin portion, which therefore contains 2 difficultly esterifiable and hence *tert.* OH. Also mild acetylation transforms (**II**) into its *diacetate*, m.p. 268—269°, hydrolysed by dil. H_2SO_4 to *g-strophanthidin diacetate*, m.p. 240°. The constitution of (**I**) is therefore very probably *A*. (**III**) is most readily obtained

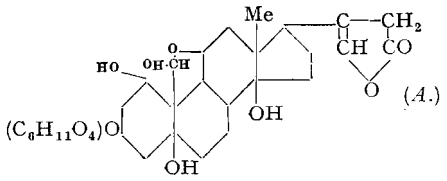


(*A.*)

by heating (**II**) in $PhNO_2$; it is not quite homogeneous since a small amount of an isomeride (?) can be extracted from it by MeOH. It is not obtained from (**IV**) by the action of acids. It adds H_2O in boiling 50% EtOH containing a little HCl with re-formation of (**IV**). Hydrogenation (PtO_2 in 50% EtOH containing MgO) of (**III**) does not proceed smoothly but appears to lead to *dihydroanhydro-g-strophanthidin* (**V**), m.p. 284—287°, which does not give the Legal reaction. With Ac_2O in boiling C_5H_5N (**III**) yields a *diacetate*, m.p. 264—265° (Legal reaction positive). A double linking in it cannot be detected by BzO_2H. In abs. EtOH it absorbs 1 mol. of H_2, giving an amorphous product with negative Legal reaction. (**V**) readily adds H_2O in presence of 40% EtOH containing HCl with formation of an isomeric *dihydro-g-strophanthidin*, m.p. 230—231°. H. W.

Two dehydrogenation products of *g*-strophanthin (ouabain). C. Mannich and G. Siewert (*Ber.*, 1942, **75**, [*B*], 750—755).—Oxidation of *g*-strophanthidin (**I**) by O_2 in presence of PtO_2–H_2O leads to α- (**II**) and β- (**III**) *-dehydro-g-strophanthin*. The change is regarded as consisting in the oxidation of $CH_2{\cdot}OH$ to CHO which then forms a lactol with development of an additional asymmetric centre (cf.

A). (**II**), m.p. 232—236°, $[\alpha]_D^{22}$ −63·5° in abs. EtOH, is very hygroscopic and gives a *trihydrate*. The Legal reaction is positive.



It does not react with magenta–H_2SO_3 or with reagents for :CO. Its reducing power towards cold Fehling's solution is ~5 times that of (**I**). In H_2O containing PtO_2 it absorbs 2 H_2, giving a product (+~$2H_2O$), m.p. 278—279°, $[\alpha]_D^{20}$ −45·33° in H_2O. (**II**) is hydrolysed by HCl–$COMe_2$ to the *anhydrogenin*, $C_{23}H_{30}O_7$ (Legal reaction positive), and rhamnose (**IV**). (**III**) has m.p. 210—212°, $[\alpha]_D^{22}$ −27·82° in H_2O, is very hygroscopic, and affords a *tetrahydrate*. It strongly reduces cold Fehling's solution and Ag_2O–NH_3. It slowly absorbs 2 H_2 giving a product with negative Legal reaction which is possibly identical with dihydro-ouabain. (**III**) is hydrolysed by HCl–$COMe_2$ to (**IV**) and *β-dehydroanhydro-g-strophanthidin*, m.p. 258—260°, which gives a positive Legal reaction. H. W.

End-group assay for laminarin and similarly constituted polysaccharides. V. C. Barry (*J.C.S.*, 1942, 578—581).—Laminarin (**I**) with Br in H_2O is oxidised to a small but definite extent. With HIO_4 it yields, by fission of the end-group, a dialdehydic product (**II**), further oxidised (Br) to laminarinic acid (**III**) [identical with that obtained from (**II**) after preliminary oxidation with Br]. Analysis of the Ag salt of (**III**), allowance being made for the extra oxidation by Br, shows that (**I**) has a chain length of 16 units. On hydrolysis (**II**) yields $(CHO)_2$, whilst (**III**) yields CHO·CO_2H, oxidised to $H_2C_2O_4$. A. Li.

Constitution of arabogalactan. III. Location of the arabinose component. E. V. White (*J. Amer. Chem. Soc.*, 1942, **64**, 1507—1511; cf. A., 1942, II, 219).—Hydrolysis of arabogalactan (**I**) (from larch sawdust), best effected by 0·02N-H_2SO_4 (too rapid with >0·05N- and too slow with 0·01N-acid) at 100°, removes most of the arabinose (**II**) before much affecting the galactose chain, but complete separation is impossible; after 23 hr. [6·16% of residual (**II**); 88·4% of residual polysaccharide] the product is treated with 30% NaOH–Me_2SO_4 at 25° and then 2% dry HCl–MeOH at 115°, which yields methyltrimethylarabinoside (1·0 mol.), methyl-tetra- (1·82), -tri- (*A*) (1·14), and -di-methylgalactoside (3·04 mols.), the ratios becoming 0 : 1·97 : 2·01 : 2·02 when allowance is made for unchanged (**I**). Hydrolysis (N-H_2SO_4; 100°) of (*A*) yields 2 : 3 : 6- (**III**) and 2 : 3 : 4-trimethylgalactose (**IV**), the latter only being formed if preliminary partial hydrolysis is omitted. It follows that the (**II**) is linked at $C_{(1)}$ to $C_{(6)}$ of a galactose mol. which is linked also to two other galactose units. (**IV**) is separated as CPh_3 ether from (**III**), which is then isolated as anilide. R. S. C.

Carbohydrate residue in ovomucoid. II. M. Stacey and J. M. Woolley (*J.C.S.*, 1942, 550—555; cf. A., 1940, II, 120).—Ovomucoid with NaOH–Me_2SO_4, then Ag_2O–MeI, yields a methylated carbohydrate residue hydrolysed (4% HCl) to *N*-acetyl-3 : 4 : 6-trimethylglucosamine (7 mols., isolated by condensation with *o*-OH·C_6H_4·CHO, and *d*-mannopyranose (2 mols.), 3 : 4 : 6-trimethyl-*d*-mannopyranose (1 mol.), and 2 : 3 : 4 : 6-tetramethyl-*d*-galactopyranose (1 mol.), separated by acetylation, glycoside formation, and fractionation. It is concluded that the carbohydrate has a core of 3 mannose units, to which are attached by glycosidic links 1 galactose and 7 *N*-acetylglucosamine units. A. Li.

Mol. wts. of the Schardinger α- and β-dextrins. D. French and R. E. Rundle (*J. Amer. Chem. Soc.*, 1942, **64**, 1651—1653).—By *X*-ray diffraction and crystal *d*, Schardinger's α- and β-dextrins are shown to contain 6 and 7 glucose units, respectively, and are renamed cyclo-*hexa*- and -*hepta-amylose*, respectively. R. S. C.

Distribution of acetyl groups in a technical acetone-soluble cellulose acetate. T. S. Gardner and C. B. Purves (*J. Amer. Chem. Soc.*, 1942, **64**, 1539—1542).—The rate of interaction of commercial $COMe_2$-sol. cellulose acetate (**I**) (Ac ~39·7%) (A., 1940, II, 69) with *p*-C_6H_4Me·SO_2Cl in C_5H_5N at 20±5° and the amount of interaction with NaI in $(COMe·CH_2)_2$ at 120° are determined (cf. A., 1942, II, 167). Rates of esterification are 23·4, 2·16, and 0·106 for OH on $C_{(6)}$ and in the second and third positions of the C_6 chain, respectively. Oxidation by $Pb(OAc)_4$ shows substantial absence of $C_{(2)}$–$C_{(3)}$ glycol units. (**I**) contains 0·198, 0·139, and 0·223 free OH at $C_{(6)}$, $C_{(2)}$, and $C_{(3)}$, respectively. R. S. C.

III.—HOMOCYCLIC.

Preparation of *cyclo*propane.—See B., 1942, II, 312.

Dehydrogenation. II. *spirocyclo*Pentane-1 : 1′-tetrahydronaphthalene. M. Levitz and M. T. Bogert (*J. Amer. Chem. Soc.*, 1942, **64**, 1719—1720; cf. A., 1941, II, 126).—Repeated passage of

1 : 2 : 3 : 4-tetrahydronaphthalene-1 : 1′-*spirocyclo*pentane over Pd–C (apparatus described) at 355–375° or 420—430° gives phenanthrene as sole aromatic product. R. S. C.

Orientation in the alkylation of *m*-xylene by various procedures and reagents. (Miss) D. Nightingale, H. D. Radford, and O. G. Shanholtzer (*J. Amer. Chem. Soc.*, 1942, **64**, 1662—1665).—Contrary to earlier work (A., 1939, II, 103), *m*-xylene, $Bu^{\gamma}OH$, and 85% H_2SO_4 give a mixture (*A*) of 1 : 3 : 5- (2 pts.) and 1 : 3 : 4-$C_6H_3Me_2Bu^{\gamma}$ (1 pt.) [(*NHAc*)$_2$-derivative, m.p. 331°], the former product being also obtained by $Bu^{\gamma}OH$–75% H_2SO_4 or –BF_3 and by $Bu^{\gamma}Cl$–$FeCl_3$. CMe_2Et·OH–85% H_2SO_4 or –BF_3 gives a mixture (*B*) [including the abnormal (1 : 3 : 5) product], but *sec.*-BuOH–85% H_2SO_4 or –BF_3 gives, normally, 1 : 3 : 4-$C_6H_3Me_2$·$CHMeEt$. Structures are proved by oxidation of the *tert.* hydrocarbons by $KMnO_4$ in aq. C_5H_5N at ~80° to 5- (**I**), m.p. 343° (sealed tube) (*Me*$_2$ ester, m.p. 97°), and 4-tert.-*butyl*- (**II**), m.p. 230°, and 5-tert.-*amyl*-isophthalic *acid* (**III**), m.p. 307° (*Me*$_2$ ester, m.p. 81°); (*B*) gives a tert.-*amyl*isophthalic *acid*, m.p. 330°; (**I**) and (**II**) obtained from (*A*) are separated by solubility of (**II**) and not of (**I**) in aq. C_5H_5N. (**I**) and (**III**) are also obtained by boiling $AcCO_2H$ with $Bu^{\gamma}CHO$ or CMe_2Et·CHO (prep. from CMe_2Et·MgCl and HCO_2Me at −50° to −55°), respectively, in aq. $Ba(OH)_2$. 2 : 4 : 1-$C_6H_3Me_2$·COMe and MgEtBr give a carbinol, dehydrated by H_2SO_4–Ac_2O to an olefine, b.p. 102°/1 mm., which with H_2–Raney Ni in MeOH at 80—90°/2000 lb. gives 1 : 3 : 4-$C_6H_3Me_2$·$CHMeEt$, b.p. 82°/1 mm., and thence 4-sec.-*butyl*isophthalic *acid*, m.p. 188°. Chloromethylation etc. gives 2 : 4-*dimethyl*-6-sec.-, b.p. 115°/1 mm., -6-tert.- (**IV**), b.p. 111—116°/1 mm., -5-n-, b.p. 103—108°/1 mm., and -5-sec.-, b.p. 100—106°/4 mm., -*butylbenzyl chloride* and thence the *alcohols*, b.p. 158—162°/14 mm., (**V**), m.p. 99°, b.p. 135—140°/? mm., and b.p. 145—150°/10 mm., respectively. With NH_2Ac at 210°, (**IV**) gives N-2 : 4-*dimethyl*-6-tert.-*butylbenzylacetamide*, m.p. 197°. $KMnO_4$ at 0—20° converts (**V**) into 2 : 4 : 6 : 1-$C_6H_2Me_2Bu^{\gamma}$·CO_2H. R. S. C.

Diphenyl and its derivatives. XXI. Passage from the diphenyl to the fluorene system. Synthesis of 2 : 7-dimethylfluorene. XXII. Synthesis of 2 : 6-dimethylfluorene. XXIII. Synthesis of 3 : 5-dimethylfluorene. L. Mascarelli and B. Longo (*Gazzetta*, 1941, **71**, 289—293, 293—297, 297—301).—XXI. 1 : 3 : 4-$C_6H_3Me_2I$ and 1 : 4 : 3-C_6H_3MeI·NO_2 (**I**) with Cu powder at 250—260° (bath) give 2′-*nitro*-2 : 4 : 4′-*trimethyldiphenyl*, an oil, reduced by $SnCl_2$–HCl–AcOH to the hydrochloride of the 2′-NH_2-compound, which when diazotised and decomposed (40—50°) gives 2 : 7-*dimethylfluorene*, m.p. 114—115°.

XXII. Similarly 1 : 4 : 2-$C_6H_3Me_2I$ (**II**) and (**I**) give, with *p*-xylene (**III**) and 2 : 5 : 2′ : 5′-tetramethyldiphenyl (**IV**) (new m.p. 52—53°), 2′-*nitro*-2 : 5 : 4′-*trimethyldiphenyl*, an oil, which gives the 2′-NH_2-compound, diazotised and converted into 2 : 6-*dimethylfluorene*, m.p. 66—66·5°. A by-product in the prep. of (**II**) by the method of Varma *et al.* (A., 1935, 1229), 1 : 4 : 2 : 5-$C_6H_2Me_2I$·NO_2, is reduced to 5-*nitro*-p-2-*xylidine hydrochloride*, m.p. (+$2H_2O$) 224—225° (decomp.).

XXIII. Similarly 1 : 2 : 3-C_6H_3MeI·NO_2 and (**II**) give, with (**III**) and (**IV**), 2′-*nitro*-, m.p. 72—73°, reduced to 2′-*amino*-2 : 5 : 6′-*trimethyldiphenyl* [*hydrochloride*, m.p. 184—185° (sinters 175—176°)], which on diazotisation and decomp. gives (in small yield) 3 : 5-*dimethylfluorene*, m.p. 81—82°. E. W. W.

Determination of the angle between the phenyl groups in αα-diphenylethylene from electric dipole moment measurements. G. E. Coates and L. E. Sutton (*J.C.S.*, 1942, 567—570).—See A., 1942, I, 387. The following are described: *p*-C_6H_4Br·$CPh{:}CH_2$, m.p. 25·5—26·0° (corr.) (lit., an oil); (*p*-$C_6H_4Cl)_2C{:}CH_2$, new m.p. 86·2—86·5° (corr.); αα-*di*-p-*bromo*-, m.p. 85·8—86·2° (corr.) [from $CO(C_6H_4Br$-*p*$)_2$], and αα-*di*-p-*fluoro-phenylethylene*, b.p. 137·5—138·5° (corr.)/12 mm., m.p. 46·5—47·0° (corr.) [from the diazonium borofluoride from $CH_2(C_6H_4·NH_2$-*p*$)_2$ by way of *pp′-difluorodiphenylmethane*, b.p. 263·5° (corr.)/754 mm., m.p. 27·0—27·4°, and $CO(C_6H_4F$-*p*$)_2$].

Synthetic [pharmacologically] active products. I. New synthesis of symmetrical diaryldialkylethylene compounds. L. von Vargha and E. Kovács (*Ber.*, 1942, **75**, [*B*], 794—802).—*p*-Methoxypropiophenonehydrazone, m.p. 74—76° (lit. m.p. 60°), is oxidised by HgO in light petroleum at 18—20° to *p*-anisylethyldiazomethane, immediately converted by SO_2 into the very unstable *trans-αβ*-di-*p*-anisyl-*αβ*-diethylene sulphone, which passes at 80—100° and subsequently at 120° into *trans-αβ*-di-*p*-anisyl-*αβ*-diethylethylene, m.p. 123—124°, converted by KOH–EtOH into diethylstilbœstrol (**I**). p-*Bromopropiophenoneazine*, m.p. 112°, is transformed by N_2H_4 at 120—130° into p-*bromopropiophenonehydrazone*, m.p. 35°, which passes when treated successively with HgO and SO_2 and then heated into αβ-*di*-p-*bromophenyl*-αβ-*diethylethylene* [γδ-*di*-p-*bromophenyl*-Δ$^{\gamma}$-*hexene*], trans-*form* (**II**), m.p. 125°, cis-*variety* (**III**), m.p. 74°. (**II**) is converted by KOH in MeOH or EtOH at 180—190° into trans-αβ-*diphenyl*-αβ-*diethylethylene*, b.p. 165°/14 mm., m.p. 76°, also obtained from propiophenonehydrazone, b.p. 88°/1 mm., derived from the corresponding *azine*, m.p. 68°. (**II**) or (**III**) is transformed by 20% NH_3–H_2O containing CuI at 150° into trans-αβ-*di*-p-*aminophenyl*-αβ-*diethylethylene* (**IV**), m.p. 132° (*hydrochloride*, decomp.

220°; normal *sulphate*, decomp. >210°; Ac_2 derivative, m.p. >300°), converted through the diazo-compound into (**I**). At 150° in presence of dil. NH_3 containing CuI (**III**) is partly isomerised to (**II**). (**IV**) is converted by HNO_2 followed by $HgBr_2$ and heating of the compound with NaBr into (**II**). The œstrogenic activity of these ethylenes is very slight in comparison with that of diethylstilbœstrol dipropionate so that the presence of phenolic OH appears essential to the development of strong physiological action. H. W.

αω-Diphenyl compounds with long chains. A. W. Schmidt and A. Grosser (*Ber.*, 1942, **75**, [*B*], 826—829).—The m.p. curves of αω-Ph_2 compounds with long chains pass through a min. when 12—14 C are present in the chains. αω-Dicarboxylic acids with long chains are converted into their chlorides and thence (Friedel–Crafts) into the ketones. These do not appear to be smoothly reduced by N_2H_4 and NaOAlk but are transformed by $Al(OPr^{\beta})_3$ into the saturated diols; these afford the corresponding dienes which are hydrogenated (Pd–$BaSO_4$) to the saturated hydrocarbons. The following are described: *αζ-diphenyl-hexane-αζ-diol*, m.p. 133·5°, -$\Delta^{\alpha\epsilon}$-*hexadiene*, m.p. 81°, and *-hexane*, m.p. 72°; *aκ-diphenyl-decane-aκ-diol*, m.p. 72°, -$\Delta^{\alpha\iota}$-*decadiene*, m.p. 53°, *-decane*, b.p. 169—170°/0·03 mm., m.p. 17·5° and *aκ-dicyclohexyldecane*, b.p. 158°/0·03 mm., m.p. 33·5—34·5°; *aσ-diphenyl-octadecane-aσ-dione*, m.p. 101°, *-octadecane-aσ-diol*, m.p. 76°, -$\Delta^{\alpha\beta}$-*octadecadiene*, m.p. 93°, and *-octadecane*, m.p. 61°. H. W.

Isomeric phenyldodecenes and phenyldodecanes. A. W. Schmidt and A. Grosser (*Ber.*, 1942, **75**, [*B*], 829—833).—Long, normal chains have a much more favourable influence on the viscosity relationships of compounds than have branched chains. The η–temp. relationship is much more dependent on small changes in constitution than are other physical data. The requisite alcohols are obtained by the action of Mg *n*-alkyl chlorides on Ph alkyl ketones, the reactants being so paired that the sum of the C atoms in the two straight chains is 12. They cannot be isolated since they are not cryst. and lose H_2O when distilled in a vac. They are dehydrated by $KHSO_4$ at 120—160° to mixtures of dodecenes which are hydrogenated (Pd–$BaSO_4$) to homogeneous dodecanes. The following are described: β-, b.p. 125°/0·8 mm., γ-, b.p. 145—146°/2·0 mm., δ-, b.p. 118—120°/0·8 mm., ε-, b.p. 131—132°/1·0 mm., and ζ-, b.p. 127°/1·0 mm., -phenyldodecene: β-, b.p. 143°/8 mm., γ-, b.p. 127°/0·8 mm., δ-, b.p. 140—142°/0·8 mm., ε-, b.p. 113°/0·4 mm., and ζ-, b.p. 108°/0·4 mm., —, *-phenyldodecane*. Vals. of η at 20°, 30°, 40°, 50°, 60°, 70°, and 80°, of n_D^{20}, and of d_4^{20} and d_4^{30} for the hydrocarbons are tabulated. H. W.

Preparation of 1 : 2 : 4 : 5-tetraphenylbenzene from benzylideneacetophenone. A. Schönberg and A. F. A. Ismail (*J.C.S.*, 1942, 585).—CHPh:CH·COPh with $(COCl)_2$ at the b.p. yields CHPhCl·CH:CPhCl, converted by KI in boiling $COMe_2$ into αζ-dichloro-αγδζ-tetraphenyl-$\Delta^{\alpha\epsilon}$-hexadiene, m.p. 159—160° (decomp.) (cf. Strauss *et al.*, A., 1925, i, 534). Thermal decomp. of this (200°) yields 1 : 2 : 4 : 5-$C_6H_2Ph_4$ almost quantitatively. A. Li.

Dissociation of hexa-arylethanes. XIII. Halogen substituents. C. S. Marvel, F. C. Dietz, and C. M. Himel (*J. Org. Chem.*, 1942, **7**, 392—396).—The degrees of dissociation of di-*o*- and -*p*-fluoro-, di-*o*-, -*m*-, and *p*-chloro-, di-*o*-, -*m*-, and -*p*-bromo-, and di-*p*-iodohexaphenylethane have been measured by the magnetic susceptibility method. The order of effectiveness in producing dissociation is *o*- > *m*- > *p*-halogen; in the *o*-position the order is Br > Cl > F. In general, halogen substituents in C_2Ph_6 appear to have about the same influence on dissociation as dialkyl substituents. The following are new: *diphenyl*-m-*chloro-*, m.p. 53—55°, and -p-*iodo-*, m.p. 73—74°, *-phenylcarbinol*; p-*chlorophenyldi*-p-*bromophenylcarbinol*, m.p. 115—116°; *diphenyl*-m-*chlorophenylmethyl chloride*, m.p. 55—57°. The following *peroxides*: *diphenyl*-o-*fluorophenylmethyl*, m.p. 155—156°, *diphenyl*-m-*chlorophenylmethyl*, m.p. 159—160°, *diphenyl*-o-*bromophenylmethyl*, m.p. 145—146°, and p-*chlorophenyldi*-p′p″-*bromophenylmethyl*, m.p. 194—195°. H. W.

Nitrovinylnaphthalene. D. E. Worrall and A. Tatilbaum (*J. Amer. Chem. Soc.*, 1942, **64**, 1739—1740).—β-$C_{10}H_7$·CHO and $MeNO_2$ in NaOH–EtOH gives 2-*α-nitrovinylnaphthalene*, m.p. 120·5—122° (with Br–$CHCl_3$ gives an *α-Br*-derivative, m.p. 107—108°). In presence of aliphatic amines, a *polymeride*, $(C_{12}H_9·NO_2)_x$, m.p. ~253° (decomp.), is formed. R. S. C.

Synthesis of vetivazulene.—See A., 1942, II, 417.

***N*-Substituted derivatives of phosphoryl and thiophosphoryl triamide as hydrogen bonding agents.**—See A., 1942, I, 406.

Properties of anils. T. F. West (*J.S.C.I.*, 1942, **61**, 158—159).—The relative toxicities to *Protocalliphora azurea* of some anils (CHR:NR′) are recorded. *Furfurylidene-*, b.p. 118—119°/2 mm., and *benzylidene-β-hydroxyethylamine*, m.p. 23—24°, b.p. 128—130°/2 mm., and *citronellylidene-aniline*, b.p. 130—133°/2 mm., α_D +7·3°, -cyclo*hexylamine*, b.p. 137—139°/2 mm., α_D +3·3°, and *-β-hydroxyethylamine*, b.p. 110—115°/2 mm., α_D +2·1°, are described. (All α are for $l = 1$.) T. F. W.

Reactions of furan compounds. I. Constitution of the coloured condensation product from furfuraldehyde, aniline, and aniline hydrochloride. G. Williams and C. L. Wilson (*J.C.S.*, 1942, 506—507).—The product (**I**) from furfuraldehyde (**II**) and NH_2Ph in EtOH–conc. HCl is NHPh·CH:CH·CH:C(OH)·CH:NPh,HCl, since, contrary to Riegel *et al.* (A., 1941, II, 330), HNO_2 causes cleavage to NH_2Ph and thence yields PhN_2Cl. The product from (**II**) and *p*-$C_6H_4Me·NH_2$ similarly gives *p*-$C_6H_4Me·N_2Cl$. Further, (**I**) is obtained in poor yield from $NPhMe_2$ and NH_2Ph,HCl in MeOH (cf. *loc. cit.*). R. S. C.

Interaction of dimethylaniline and nitric acid. H. H. Hodgson and G. Turner (*J.C.S.*, 1942, 584—585).—Oxidation and nitration of $NPhMe_2$ (**I**) occur with excess of HNO_3 (*d* 1·12) at 0°; 3 : 5 : 3′ : 5′-tetranitrotetramethylbenzidine (40%) (**II**), new m.p. 273° (decomp. 275°), and (mainly) 2 : 4 : 1-$(NO_2)_2C_6H_3·NMe_2$ (60%) (**III**) result. Nitration predominates with increase in *d* of HNO_3, and is accompanied (also at higher temp.) by expulsion of Me. (**I**) and HNO_3 (*d* 1·52) at −5° to 0° give 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2·NMe·NO_2$, whilst (**I**) or (**III**) and HNO_3 (*d* 1·42) at 0° give 2 : 4 : 6 : 1-$(NO_2)_3C_6H_2·NHMe$; at room temp. (**I**) yields 2 : 4 : 1-$(NO_2)_2C_6H_3·NHMe$ (**IV**) and (**III**). With HNO_3 (*d* 1·34 or 1·254) at 0°, (**I**) affords (**III**) (after 30—60 min.), but on keeping (or at higher temp.) (**IV**) [or (**IV**) and some (**III**)] results. Addition of $NaNO_2$ accelerates the above reactions, but with HNO_3 (*d* 1·12), the yield of (**II**) falls to ~2·5%, and some *p*-$NO_2·C_6H_4·NMe·NO$ is formed. (**I**) and HNO_3 (*d* 1·046 and 1·024) do not react at room temp. (2 weeks), but on adding $NaNO_2$, *p*-$NO·C_6H_4·NMe_2$ (**V**) (pptd. as nitrate) and a little *p*-$NO_2·C_6H_4·NMe_2$ are formed; excess of $NaNO_2$ yields (**V**) with some 3 : 3′-dinitrotetramethylbenzidine and *p*-$NO_2·C_6H_4·NHMe$. (**V**) and HNO_3 (*d* 1·42) at 0° give (**III**), and at higher temp., (**IV**). HNO_3 (*d* 1·42) expels the Me groups from 3 : 5 : 3′ : 5′-tetranitrodimethylbenzidine. A. T. P.

Application of the bromometric assay. II. Bromination of derivatives of aminobenzenesulphonic acids. E. H. Wells (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 747—755).—M.p., bromination factors, and m.p. of Br-derivatives are given for $NH_2·C_6H_4·SO_3H$ and derivatives of therapeutic importance. Details of procedure are recorded. *p*-$NH_2·C_6H_4·SO_2·NHAc$ ("sulamyd") affords a Br_2-derivative, m.p. 193·8—194·6°. A. A. E.

Mercuric derivatives of *p*-aminobenzenesulphonamide. M. Ragno and (Signa.) C. Solarino (*Gazzetta*, 1941, **71**, 235—242).—*p*-$NH_2·C_6H_4·SO_2·NH_2$ (**I**) with $Hg(OAc)_2$ in aq. EtOH gives an ill-defined product, but with $HgCl_2$–Na_2CO_3 in H_2O gives a *compound*, $(C_6H_6O_2N_2SHg)_x$ (**I**), converted by aq. Br–KBr into 4 : 3 : 5-$NH_2·C_6H_2Br_2·SO_2·NH_2$, which with $HgCl_2$–KOH forms a *compound*, $(C_6H_4O_2N_2Br_2SHg)_x$ (**II**). It is suggested that in these compounds $x = 1$ or 2, Hg being linked to the NH groups. Hg is removed from (**I**) or (**II**) by aq. $Na_2S_2O_3$ or KI. With Br, (**II**) gives 2 : 4 : 6-$C_6H_2Br_3·NH_2$. E. W. W.

Chemotherapy. V. Sulphanilylcyanamide and related compounds. P. S. Winnek, G. W. Anderson, H. W. Marson, H. E. Faith, and R. O. Roblin, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 1682—1685; cf. A., 1942, II, 272).—Addition of *p*-NHAc·$C_6H_4·SO_2Cl$ (**I**) to aq. $CaCN_2$, kept alkaline by NaOH, at 25—30° gives *Ca acetylsulphanilylcyanamide* (**II**) (73%), hydrolysed by boiling 10% NaOH to *sulphanilylcyanamide*, m.p. 292—295°, which is also obtained by condensing *p*-$NO_2·C_6H_4·SO_2Cl$ (**III**) with $CN·NH_2$ and subsequent reduction by Fe powder in 5% AcOH. In 4N-HCl at 100°, (**II**) gives *sulphanilylcarbamide* (82%), m.p. 140—144°. *Sulphanilylmethylisocarbamide*, m.p. 172—173°, is obtained (*a*) from *p*-$NO_2·C_6H_4·SO_2·NNa·CN$ by HCl–MeOH and then Fe–AcOH, (*b*) (**II**) and HCl–MeOH, and (*c*) (**III**) and $NH_2·C(OMe):NH$,HCl (later reduction). Method (*a*) gives also *sulphanilylethylisocarbamide*, m.p. 126—127°. $NH_2·C(SR):NH,H_2SO_4$ with (**I**) and then boiling conc. HCl–EtOH gives *sulphanilyl-methyl-* (**IV**), m.p. 184—185°, and *-ethyl-isothiocarbamide*, m.p. 154—155°. NHAlk·$C(NH_2):NH,H_2SO_4$ with (**I**)–NaOH–$COMe_2$–H_2O at 18—22° and then boiling 4N-HCl gives *sulphanilyl-ethyl-*, m.p. 160—161°, *-propyl-*, m.p. 147—148°, and *-butyl-guanidine*, m.p. 184—186° [also obtained from the Ac derivative of (**IV**) by boiling NH_2Bu–50% EtOH and then HCl–EtOH–H_2O]; similarly are prepared *sulphanilyl-nitroguanidine* (**V**), m.p. 194—195°, *-dicyanodiamide*, m.p. 236—237°, *-guanylcarbamide*, m.p. 225—226°, *-diguanidine*, m.p. 244—245°, *-butyldiguanidine*, m.p. 214—215°, *-dimethyldiguanidine*, m.p. 191—192°, and *-o-tolyldiguanidine* (**VI**), m.p. 214—216°. *Sulphanilylphenylguanidine*, m.p. 231—233°, is obtained from the Ac derivative of (**V**) by NH_2Ph in boiling dioxan and then HCl [this method gives also (**VI**)] and from (**II**) by NHPhAc and then HCl; the latter method gives also *sulphanilyl*-p-*aminophenyl-*, m.p. 200—201°, -p-*carboxyphenyl-*, m.p. 234—235°, and -2-*pyridyl-guanidine*, m.p. 239—241°. *Sulphanilylaminoguanidine* (**VII**), m.p. 209—210° (N^4-*Ac* derivative, m.p. 256—257°), is obtained from the Ac derivative of (**IV**) by N_2H_4 and then HCl, and by Fe-reduction of (**V**). M.p. are corr. with decomp. Solubility in H_2O and NaOH, max. blood level, and *in vitro* activity are recorded for the products. Use of sulphanilylguanidine (**VIII**) (m.p. 189—190°) etc. as intestinal agents depends on their poor absorption and low max. blood level. The above-named guanidine derivatives, unless alkylated, are poorly absorbed but only (**VII**) exceeds (**VIII**) in activity *in vitro* against *B. coli*. R. S. C.

Formation and behaviour of aryl aminophenylcarbamates. L. C. Raiford, E. Conrad, and W. H. Coppock (*J. Org. Chem.*, 1942, **7**, 346—353).—$NO_2{\cdot}C_6H_4{\cdot}NH_2$ (2 mols.) is treated in dry Et_2O at room temp. with $ClCO_2Ar$, thus giving *Ph* o-, m-, and p-, m.p. 98—99°, 123—124°, and 165—166°, respectively, and o-C_6H_4Cl o-, m-, and p-*nitrophenylcarbamate*, m.p. 113—115°, 136—137°, and 154—155°, respectively, and *Ph* 4-*nitro*-m-*tolylcarbamate*, m.p. 128—130°. Reduction ($SnCl_2$ and HCl) gives *Ph* o- (**I**), m-, and p-, m.p. 157—158° (decomp.), 178—179°, and 134—135°, respectively, and o-C_6H_4Cl m-, m.p. 160° (decomp.), and p-*aminophenylcarbamate*, m.p. 140° (decomp.) (hydrochlorides). Ph_2 o-, m-, and p-, m.p. 189—190°, 163—165°, and 238—239°, respectively, and *di*-o-*chlorophenyl* o-, m-, and p-NN′-*phenylenedicarbamate*, m.p. 170° (softens at 140°), 201—202°, and 223—224°, respectively, are described. Substituted phenylenediamines, $NHR{\cdot}C_6H_4{\cdot}NHR'$, are described as follows: *o*-series: R = *Ac*, R′ = CO_2Ph, m.p. 143—144°; R = *Bz*, R′ = CO_2Ph, m.p. 146—148°; R = *Ac*, R′ = $CO_2{\cdot}C_6H_4Cl$-*o*, m.p. 125—126°; R = *Bz*, R′ = $CO_2{\cdot}C_6H_4Cl$-*o*, m.p. 145—147°; *m*-series: R = *Ac*, R′ = CO_2Ph, m.p. 144—146°; R = *Bz*, R′ = CO_2Ph, m.p. 157—158°, R = *Ac*, R′ = $CO_2{\cdot}C_6H_4Cl$-*o*, m.p. 175—176°; R = *Bz*, R′ = $CO_2{\cdot}C_6H_4Cl$-*o*, m.p. 170—171°; *p*-series, R = *Ac*, R′ = CO_2Ph, m.p. 175—176°; R = *Bz*, R′ = CO_2Ph, m.p. 223°; R = *Ac*, R′ = $CO_2{\cdot}C_6H_4Cl$-*o*, m.p. 182—183°; R = *Bz*, R′ = $CO_2{\cdot}C_6H_4Cl$-*o*, m.p. 195—196°. (**I**) is converted by 10% KOH into *o*-$C_6H_4(NH)_2CO$, m.p. 300—303°, also obtained from *o*-C_6H_4Cl *o*-aminophenylcarbamate hydrochloride in an attempt to secure the free base.

H. W.

Azoyl derivatives of sugars.—See A., 1942, II, 395.

Decomposition of zinc chloride double salts of diazonium compounds by alcohols and phenols. H. H. Hodgson and C. K. Foster (*J.C.S.*, 1942, 581—583).—MeOH or EtOH decomposes $(ArN_2Cl)_2,ZnCl_2$ (**I**) (Ar = α- and β-$C_{10}H_7$; *o*- and *p*-C_6H_4Me; *o*- and *p*-C_6H_4Cl; *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4$) normally, and N_2Cl is replaced by H or OAlk according to the nature of the substituents in Ar (except in presence of Zn dust when H replacement is the sole change). With PhOH at 60° (or ~130° in some cases) (**I**) afford (mainly) ArCl with some *p*-$C_6H_4Ar{\cdot}OH$ and PhOAr; proportions of each from (**I**) (Ar = *p*-$OH{\cdot}C_6H_4$; *p*-$OMe{\cdot}C_6H_4$; *p*-C_6H_4Cl; Ph; α- and β-$C_{10}H_7$) are recorded; when Ar is *o*-, *m*-, or *p*-$NO_2{\cdot}C_6H_4$ formation of $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH$ occurs at <90°. 4-*Chloro*-4′-*acetoxydiphenyl* has m.p. 72°. Reaction mechanisms are discussed.

A. T. P.

Complexes of titanium with aromatic hydroxy-compounds, and its photometric determination with chromotropic acid.—See A., 1942, I, 410.

Acylation of phenols in presence of magnesium and preparation of phenolic esters. A. Spassow (*Ber.*, 1942, **75**, [*B*], 779—780).—The phenol (0·1 mol.) in C_6H_6 (20—25 g.), Mg turnings (1·2 g. Mg for each OH in 0·1 mol. of phenol), and AcCl (0·1—0·12 mol.) are heated at ~90° for 0·5—1 hr. The following esters are obtained in % yields indicated in parentheses: Ph acetate, b.p. 75—76°/8 mm. (92), propionate, b.p. 100°/16 mm. (92), *n*-butyrate, b.p. 106·5°/13 mm. (98%), phenylacetate, m.p. 39—40° (93), and benzoate, m.p. 69—70° (93); *o*-tolyl acetate, b.p. 93°/12 mm. (98), and *iso*butyrate, b.p. 107—108°/8 mm. (98); *p*-$C_6H_4Me{\cdot}OAc$, b.p. 93°/10 mm. (93); thymol acetate, b.p. 119°/12 mm., and *n*-butyrate, b.p. 128°/8 mm. (97); *p*-$NO_2{\cdot}C_6H_4{\cdot}OAc$, m.p. 81—82°; *m*-, b.p. 153—154°/12 mm. (92), and *p*-$C_6H_4(OAc)_2$, m.p. 119—120° (95); 1 : 3 : 5-$C_6H_3(OAc)_3$, m.p. 104—105° (71); α-$C_{10}H_7$ acetate, m.p. 46—47° (96), and *iso*butyrate, b.p. 164—166°/9 mm. (93); β-$C_{10}H_7{\cdot}OAc$, m.p. 69—70° (96).

H. W.

Condensation of secondary aliphatic alcohols with benzene in presence of aluminium chloride. R. C. Huston and I. A. Kaye (*J. Amer. Chem. Soc.*, 1942, **64**, 1576—1580).—$Pr^{\beta}OH$, *sec.*-BuOH, or $CHMeBu^{\gamma}{\cdot}OH$ with C_6H_6 and $AlCl_3$–HCl at 0° gives, without rearrangement, cumene, *sec.*-BuPh, and γ-phenyl-ββ-dimethyl-*n*-butane, b.p. 205—207° [p-NO_2-, b.p. 117—123°/2 mm., *p*-NH_2-, b.p. 115—118°/2 mm., and p-*OH*-compound, m.p. 122°, b.p. 115—118°/3 mm. (α-*naphthylurethane*, m.p. 109—110°)], respectively. Rearrangement to *tert.*-alkyl occurs with $CHMePr^{\beta}{\cdot}OH$, $CHEtPr^{\beta}{\cdot}OH$, $CHPr^{\alpha}Pr^{\beta}{\cdot}OH$, and $CHMeEt{\cdot}CHEt{\cdot}OH$, which give β-phenyl-β-methyl-*n*-butane, b.p. 188·5—190° [*p*-NO_2-, b.p. 113—118°/2 mm., p-NH_2-, b.p. 99—103°/2 mm., and *p*-OH-derivative, m.p. 89—90°, b.p. 110—114°/3 mm. (α-*naphthylurethane*, m.p. 125—126·5°)], -*n*-pentane, b.p. 208—209° [*p*-NO_2-, b.p. 123·5—127°/2 mm., *p*-NH_2-, b.p. 111—113°/2 mm., and *p*-OH-derivative, b.p. 116—119°/3 mm. (α-*naphthylurethane*, m.p. 123·5—125°)], and -*n*-hexane, b.p. 225—226°/762 mm. [*p*-NO_2-, b.p. 140—146°/3 mm., *p*-NH_2-, b.p. 127—129°/3 mm., and *p*-OH-derivative, b.p. 123—127°/3 mm. (α-*naphthylurethane*, m.p. 125—126°)], and γ-phenyl-γ-methyl-*n*-hexane, b.p. 224—226°/762 mm. [*p*-NO_2-, b.p. 143—148°/3 mm., *p*-NH_2-, b.p. 124—126°/2 mm., and *p*-OH-derivative, b.p. 128—131°/3 mm. (α-*naphthylurethane*, m.p. 101—103°)], respectively. Mixtures (physical data quoted) are obtained from pentan-β- and -γ-ol, hexan-β- and γ-ol, $CHMeEt{\cdot}CHMe{\cdot}OH$, $CHMeBu^{\beta}{\cdot}OH$, heptan-β-, -γ-, and -δ-ol, β-methylhexan-δ- and -ε-ol, $CHMePr^{\alpha}{\cdot}CHMe{\cdot}OH$, and $CHEtBu^{\gamma}{\cdot}OH$, but nitration, reduction, and diazotisation give phenols the α-*naphthylurethanes* from which have m.p. 99—99·5°, 97·5—98·5°, 95—96·5°, 95—96°, 103—105·5°, 108—112°, 94·5—96·5°, 95·5—97·5°, 93·5—94°, 119—121°, 119—121°, 106—108°, and 114—115°, respectively. The following are prepared by Grignard reactions for comparison. $CHPhEt_2$, b.p. 189—191°/741 mm. [p-NO_2-, b.p. 110—115°/2 mm., p-NH_2-, b.p. 107—116°/3 mm., and *p*-OH-derivative, m.p. 75·5°, b.p. 108—117°/2 mm. (α-*naphthylurethane*, m.p. 114°)]; $CHPhMePr^{\alpha}$, b.p. 191—193°/762 mm. [p-NO_2-, b.p. 112—118°/2 mm., p-NH_2-, b.p. 101—104°/2 mm., and *p*-OH-derivative, b.p. 101—103°/2 mm. (α-*naphthylurethane*, m.p. 100—101°)]; $CHPhMeBu^{\alpha}$, b.p. 210—211°/737 mm. [p-NO_2-, b.p. 120—128°/2 mm., p-NH_2-, b.p. 112—116°/2 mm., and *p*-OH-derivative, b.p. 110—112°/2 mm. (α-*naphthylurethane*, m.p. 108—109°)]; $CHPhPr^{\alpha}_2$, b.p. 221—224° [p-NO_2-, b.p. 140—143°/2 mm., p-NH_2-, b.p. 128—132°/2 mm., and p-*OH*-derivative, b.p. 121—123°/2 mm. (α-*naphthylurethane*, m.p. 104—105°)]; $CHPhMeBu^{\beta}$, b.p. 197—198°/735 mm. [p-NO_2-, b.p. 132—133°/2 mm., p-NH_2-, b.p. 113—115°/2 mm., and p-*OH*-derivative, b.p. 109—110°/2 mm. (α-*naphthylurethane*, m.p. 107°)]; γ-p-*hydroxyphenyl*-n-*hexane*, b.p. 133°/4 mm. (α-*naphthylurethane*, m.p. 95—95·5°), -n-*heptane*, b.p. 117°/2 mm. (α-*naphthylurethane*, m.p. 100°), -ββ-*dimethyl*-n-*pentane*, b.p. 108°/2 mm. (α-*naphthylurethane*, m.p. 118—119°), and -ββ-*dimethyl*-n-*butane*, m.p. 120—121°, b.p. 123°/4 mm.; β-p-*hydroxyphenyl*-γ-*methyl*-n-*pentane*, b.p. 120—123·5°/3 mm. (α-*naphthylurethane*, m.p. 100—101°), -n-*heptane*, b.p. 140°/4 mm. (α-*naphthylurethane*, m.p. 115—116°), and -γ-*methyl*-n-*hexane*, b.p. 123—125°/2 mm (α-*naphthylurethane*, m.p. 110—111°); δ-, b.p. 111°/2 mm. (α-*naphthylurethane*, m.p. 117—117·5°), and ε-p-*hydroxyphenyl*-β-*methyl*-n-*hexane*, b.p. 123·5°/2 mm. (α-*naphthylurethane*, m.p. 125°).

R. S. C.

Condensation of resorcinol with acyclic acids. E. N. Currlin (*Anais Assoc. Quim. Brasil*, 1942, **1**, 88—95).—Review of literature.

F. R. G.

Stilbœstrol glycuronide, m.p. 175°, $[\alpha]_D^{20}$ −56·6° (1·6% in EtOH).—See A., 1942, III, 812.

Mono- and di-alkyl ethers of stilbœstrol. E. E. Reid and (Miss) E. Wilson (*J. Amer. Chem. Soc.*, 1942, **64**, 1625—1626).—Stilbœstrol (0·3; this and other figures in parentheses are *μ*g. for 1 œstrogenic rat unit), *n*-AlkBr, and NaOH–EtOH give the Me, forms, m.p. 116—117·5° and 112—114° (2·5), Me_2, m.p. 124° (20), *Et*, m.p. 99·5° or (+H_2O) 105·5—107° (5), Et_2, m.p. 127·5° (50), *Pr*, m.p. 107° (17·5), Pr_2, m.p. 95·6° (250), *Bu*, m.p. 97·5° (20), Bu_2, m.p. 101·6° (250), *amyl*, m.p. 82° (48), *diamyl*, m.p. 64·6° (600), *hexyl*, m.p. 72° (74·6), *dihexyl*, m.p. 74·6° (30,000), C_7H_{15}, m.p. 87° (45), *diheptyl*, m.p. 50·4° (750), *octyl*, m.p. 88·5° (50), *dioctyl*, m.p. 72·2° (>50,000), *nonyl*, m.p. 76° (50), *dinonyl*, m.p. 57·4° (5000), *decyl*, m.p. 75° (84), *didecyl*, m.p. 73·6° (50,000), $C_{11}H_{23}$, m.p. 58·5° (200), $(C_{11}H_{23})_2$, m.p. 66° (>40,000), $C_{12}H_{25}$, m.p. 83° (100), $(C_{12}H_{25})_2$, m.p. 80°, $C_{13}H_{27}$, m.p. 67°, $(C_{13}H_{27})_2$, m.p. 73·2°, $C_{14}H_{29}$, m.p. 85°, $(C_{14}H_{29})_2$, m.p. 86°, $C_{15}H_{31}$, m.p. 73°, $(C_{15}H_{31})_2$, m.p. 77°, $C_{16}H_{33}$, m.p. 89°, $(C_{16}H_{33})_2$, m.p. 89°, $C_{17}H_{35}$, m.p. 78·5°, $(C_{17}H_{35})_2$, m.p. 82°, $C_{18}H_{37}$, m.p. 94·3°, and $(C_{18}H_{37})_2$ *ether*, m.p. 94°.

R. S. C.

1 : 8-Dimethyl- and 2 : 7-dimethoxy-diphenylene. W. C. Lothrop (*J. Amer. Chem. Soc.*, 1942, **64**, 1698—1700).—By Atkinson's second method (A., 1941, II, 170), 3 : 1 : 2-$NO_2{\cdot}C_6H_3Me{\cdot}NH_2$ gives (6 : 2 : 1-$NO_2{\cdot}C_6H_3Me)_2$ (**I**) (24%), m.p. 107—108°, and 6 : 6′-dinitro-2 : 2′-dimethylazobenzene (**II**) (16%), m.p. 199°, the structure of (**II**) being proved by reduction (Zn dust; AcOH) to 1 : 2 : 3-$C_6H_3Me(NH_2)_2$ (*Bz*$_2$ derivative, m.p. 228—229°). (6 : 2 : 1-$NH_2{\cdot}C_6H_3MeI)_2$ [prep. from (**I**) by $SnCl_2$–HCl] gives (diazo-reaction; KI) (2 : 6 : 1-$C_6H_3MeI)_2$ (67%), pyrolysis of which with Cu_2O gives a little 1 : 8-*dimethyldiphenylene* (nomenclature, A., 1941, II, 247), m.p. 79—80° (*picrate*, m.p. 126°). *p*-$OMe{\cdot}C_6H_4{\cdot}NHAc$ and HNO_3–AcOH–H_2O at >60° give 4 : 2 : 1-$OMe{\cdot}C_6H_3(NO_2){\cdot}NHAc$, hydrolysed (HCl–EtOH–$H_2O$) to the base, the diazonium solution from which with CuOH gives [4 : 2 : 1-$OMe{\cdot}C_6H_3(NO_2)]_2$ (**III**) (64%), m.p. 131°, and [4 : 2 : 1-$OMe{\cdot}C_6H_3(NO_2){\cdot}N{:}]_2$ (5·6%), m.p. 259°. Sn–HCl–AcOH reduces (**III**) to the diamine (74%), m.p. 110°, which yields 2 : 7-dimethoxydiphenyleneiodonium iodide (77%) and thence by pyrolysis with Cu_2O 2 : 7-*dimethoxydiphenylene* (2%) (**IV**), m.p. 107—108° (*picrate*, m.p. 125°), with $(p\text{-}OMe{\cdot}C_6H_4)_2$, 2 : 2′-*diiododi*-p-*anisyl*, m.p. 131°, and 2 : 7-dimethoxyphenazone, m.p. 202—203° (lit. 197°) (*picrate*, m.p. 231—233°). Attempts to prepare the $(OH)_2$-compound from (**IV**) failed. 2 : 7-Dimethyldiphenylene picrate is obtained anhyd., having m.p. 110—111° (cf. *loc. cit.*).

R. S. C.

Resin phenols. II. Constitution of di(*iso*eugenol methyl ether). A. Müller and M. Hartai (*Ber.*, 1942, **75**, [*B*], 891—899; cf. A., 1942, II, 357).—It is shown that di(*iso*eugenol Me ether) (**I**) is 6 : 7-*dimethoxy*-1 - 3′ : 4′-*dimethoxyphenyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, its formation by dimerisation of 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}CH{:}CHMe$ being regarded as a special case of diene synthesis rendered possible by the loosening at $C_{(6)}$ caused by the *p*-OMe-group. (**I**) is oxidised by alkaline $KMnO_4$ to 3 : 4 : 3′ : 4′-tetramethoxybenzhydrol-6-carboxylactone, m.p. 187°, in poor yield. (**I**) is oxidised by CrO_3 (≡3 O) in AcOH to a small quantity of acid and, mainly, to 1(or 2)-*hydroxy*-4-*keto*-6 : 7-*dimethoxy*-1-3′ : 4′-*dimethoxyphenyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* [*hydr*-

oxyketodi(iso*eugenol Me ether*)] (**II**), m.p. 156° (*semicarbazone*, m.p. 198°), with a red-brown oil. With CrO_3 (≡5 O) the products are (**II**), veratric acid, and 3 : 4 : 3′ : 4′-tetramethoxybenzophenone-6-carboxylic acid (**III**), m.p. 220°, whilst with CrO_3 (≡8·5 O), a compound, m.p. 198°, and (**II**) are obtained (cf. Haworth *et al.*, A., 1931, 954). (**II**) is oxidised by conc. HNO_3 in aq. AcOH to 2 : 3 : 6 : 7-tetramethoxyanthraquinone and (**III**). (**II**) is converted by NaOH in warm aq. EtOH into a Na salt which gives a clear solution in a little H_2O but becomes hydrolysed on dilution with separation of 4-*hydroxy*-6 : 7-*dimethoxy*-1-3′ : 4′-*dimethoxyphenyl*-2 : 3-*dimethylnaphthalene*, m.p. 175° (*acetate*, m.p. 138°; *methanesulphonate*, m.p. 179·5°), oxidised by CrO_3 in AcOH at 15—20° to (**III**). 4 : 6 : 7-*Trimethoxy*-1-3′ : 4′-*dimethoxyphenyl*-2 : 3-*dimethylnaphthalene* has m.p. 128°. H. W.

Derivatives of 4 : 4′-diaminodiphenyl sulphone.—See B., 1942, II, 396.

Dihydroxydiphenyl sulphones. G. Machek and H. Haas [with H. Grüner, M. Novak-Arienti, J. Hilber, F. Thoma, and H. Zehe] (*J. pr. Chem.*, 1940, [ii], **160**, 41—64).—PhOMe–$SOCl_2$–$AlCl_3$ give 4 : 4′-dimethoxydiphenyl sulphide, m.p. 43—44° (also obtained from *p*-C_6H_4I·OMe, *p*-OMe·C_6H_4·SNa, and Cu at 270°), oxidised by aq. $KMnO_4$–AcOH at 100° (bath) to the sulphone, m.p. 130·4°, converted by $AlCl_3$ in boiling xylene into 4 : 4′-dihydroxydiphenyl sulphone (**I**), m.p. 245° (diacetate, m.p. 165°). PhOH and 30% oleum at 180—190° give 2 : 4′-*dihydroxydiphenyl sulphone* (**II**), m.p. 186° (*Me*$_2$ *ether*, m.p. 125°; *diacetate*, m.p. 135—136°), and (**I**). 2 : 2′-Dimethoxydiphenyl sulphide (**III**), obtained from *o*-C_6H_4I·OMe, *o*-OMe·C_6H_4·SNa, and Cu-bronze, is oxidised to the sulphone, m.p. 197°, convertible into 2 : 2′-dihydroxydiphenyl sulphone, new m.p. 191° (diacetate, new m.p. 186—188°). *p*-C_6H_4Br·OH and S_2Cl_2 yield 5 : 5′-dibromo-2 : 2′-dihydroxydiphenyl sulphide, and thence (Zn–alkali) 2 : 2′-dihydroxydiphenyl sulphide, new m.p. 138°, also obtained by demethylating (**III**). 3 : 3′-Diaminodiphenyl sulphone, m.p. 168—169°, affords 3 : 3′-*dihydroxydiphenyl sulphone* (**IV**), m.p. 192—193° (*Me*$_2$ *ether*, m.p. 88°; *diacetate*, m.p. 102°); *m*-C_6H_4I·OMe, *m*-OMe·C_6H_4·SNa, and Cu-bronze yield 3 : 3′-dimethoxydiphenyl sulphide, and thence the sulphone and (**IV**). *o*-C_6H_4I·OMe–*p*-OMe·C_6H_4·SNa, or *p*-C_6H_4I·OMe–*o*-OMe·C_6H_4·SNa, similarly give 2 : 4′-*dimethoxydiphenyl sulphide*, m.p. 45—46°, and *sulphone*, m.p. 124—125°, and thence (**II**). Similarly prepared are 2 : 3′-, m.p. 79°, b.p. 215—217°/10 mm., and 3 : 4′-*dimethoxydiphenyl sulphide*, an oil, oxidised to the *sulphones*, m.p. 122·5—123° and 89·5°, respectively, which are converted into 2 : 3′-, m.p. 127° (*diacetate*, m.p. 108·6°), and 3 : 4′-*dihydroxydiphenyl sulphone*, m.p. 163·5° (*diacetate*, m.p. 93°), respectively. A. T. P.

Action of alkali on *cyclo*hexenealdehydes. H. E. French and D. M. Gallagher (*J. Amer. Chem. Soc.*, 1942, **64**, 1497—1499).—3 : 4 : 6-Trimethyl-Δ^3-*cyclo*hexenealdehyde is converted by conc., aq. KOH or NaOH or slightly by saturated, aq. $Ba(OH)_2$ into a trimeride, m.p. 132—134°. It and related aldehydes in 1 : 2 H_2O–MeOH at 65—75° give the derived acids (~78%) and alcohols, but at >75° much polymerisation occurs. Thus are obtained 6-phenyl-3 : 4-dimethyl- (*naphthylurethane*, m.p. 110—111°), 6-methyl- (*phenylurethane*, m.p. 83°), and 3 : 4 : 6-trimethyl-Δ^3-*cyclo*hexenylmethyl alcohol (*naphthylurethane*, m.p. 112°), and Δ^3-*cyclo*hexenylmethyl alcohol (*naphthylurethane*, m.p. 106°), which are also prepared from the aldehydes by $Al(OPr^{\beta})_3$. With CH_2O–KOH–MeOH–H_2O at 70°, the aldehydes give 1 : 1-di(hydroxymethyl)-3 : 4 : 6-trimethyl-, m.p. 86·5° (*bisphenylurethane*, m.p. 121·5—123°), -6-phenyl-3 : 4-dimethyl-, m.p. 131·5° (*bisphenylurethane*, m.p. 166°), and -6-methyl-, m.p. 45° (*bisphenylurethane*, m.p. 150°), -Δ^3-*cyclo*hexene and 1 : 1-di(hydroxymethyl)-Δ^3-*cyclo*hexene, m.p. 92·5° (*bisphenylurethane*, m.p. 118·5°), which show 2 active H. With $KMnO_4$ in aq. C_5H_5N (not other solvents) at 0°, 1 : 1-di(hydroxymethyl)-*cyclo*hexane gives *cyclo*hexane-1 : 1-dicarboxylic acid. R. S. C.

β-Alkylaminoethanols.—See A., 1942, II, 394.

Decomposition of *cyclo*hexene oxide and 1 : 3-*cyclo*hexadiene from the viewpoint of the principle of least motion.—See A., 1942, I, 400.

Autoxidation of hydrocarbons. V. Secondary phenomena of the reduction of peroxides to alcohols. H. Hock and S. Lang (*Ber.*, 1942, **75**, [*B*], 313—316).—1 : 2 : 3 : 4-Tetrahydro-1-naphthyl H peroxide (**I**) is converted by aq. Na_2SO_3 into 1 : 2 : 3 : 4-tetrahydro-1-naphthol (**II**), b.p. 93—96°/0·3 mm., converted into 1 : 2-dihydronaphthalene (**III**) [dibromide, m.p. 72—73°]. (**I**) and cold $NaHSO_3$ solution afford (**III**) and (**II**) in respective yield of 30% and 35% and a small amount of *ditetrahydro*-1-*naphthyl ether* (**IV**), m.p. 84—85°. (**IV**) is obtained in 55% yield from (**II**) in Et_2O containing Na_2SO_3 and $NaHSO_3$ and passes at 180° into (**III**). (**III**) in 70—80% yield and a small proportion of (**IV**) are obtained from (**II**) with $H_2C_2O_4$, $KHSO_4$, conc. or a little 65% H_2SO_4. *cyclo*Hexenyl H peroxide and aq. Na_2SO_3 afford *cyclo*hexenol in 85% yield. *dl*-Δ^3-2-Menthenyl H peroxide is transformed by Na_2SO_3 in MeOH–H_2O into Δ^3-menthen-2-ol, b.p. 64°/0·6 mm., in 90% yield and by $NaHSO_3$ into $\Delta^{1:3}$-menthadiene and menthenol. H. W.

Hydrogenation activity of mixed nickel–copper catalysts.—See A., 1942, I, 403.

β-Hydroxy-α-phenylbutyric acid. O. Hromatka (*Ber.*, 1942, **75**, [*B*], 814—820).—CHPhAc·CO_2Et is not reduced by Al–Hg in moist Et_2O, by H_2–Pt-black–Et_2O, H_2–Pd–C–EtOH at room temp. or 54°, and only slowly by H_2–Pt-black–EtOH. In EtOH + PtO_2 it is hydrogenated to Et β-hydroxy-α-phenylbutyrate (**I**), b.p. 133°/10 Torr [p-*nitrobenzoate*, m.p. 87° (vac.)]. At 210° (**I**) passes into $CH_2Ph·CO_2Et$ and volatile substances including MeCHO isolated as the 2 : 4-dinitrophenylhydrazone. A similar fission is caused by hot dil. HCl and, particularly, by alkali. N-NaOH at room temp. hydrolyses (**I**) to the *acid*, m.p. 136°. CHPhAc·CN is converted by HCl (*d* 1·19) at room temp. into CHPhAc·$CO·NH_2$, m.p. 129—130°, reduced (H_2–PtO_2–EtOH) to β-hydroxy-α-phenylbutyramide, m.p. 113—114°; this is hydrolysed by alkali to $CH_2Ph·CO_2H$ and MeCHO. H. W.

Destruction of phenylalanine by ultra-violet radiant energy.—See A., 1942, III, 845.

Carboxylation. III.—See A., 1942, II, 393.

Preparation of esters of aromatic acids by degradation of aryl methyl ketones. G. Darzens and C. Mentzer (*Compt. rend.*, 1942, **214**, 113—115).—COArMe with HCl and *iso*-C_5H_{11}·O·NO in Et_2O at 0° yield COAr·CH:N·OH, which with dil. NaOH and Me_2SO_4 give Ar·CO_2Me in good yield. A. Li.

Local anæsthetics. I. β-Monoalkylaminoethyl alkoxybenzoates. J. S. Price, J. M. Salsbury, and J. M. Fredericksen (*J. Amer. Chem. Soc.*, 1942, **64**, 1691—1694).—OH·C_6H_4·CO_2R (1), AlkBr (1), and NaOEt (1 mol.) in boiling EtOH give *p*-OAlk·C_6H_4·CO_2Et in which Alk = Pr^{α}, b.p. 189—191°/40 mm., Bu^{α}, b.p. 196—197·5°/31 mm., *n*-amyl, m.p. 29—33°, b.p. 207—208°/30 mm., *n*-hexyl, b.p. 217—218°/30 mm., *n*-C_7H_{15}, b.p. 228—229°/30 mm., *n*-$C_{12}H_{25}$, b.p. 290—301°/45 mm., Pr^{β}, b.p. 171—177°/30 mm., Bu^{β}, b.p. 192—198°/34 mm., β-octyl, b.p. 226—229°/35 mm., and allyl, b.p. 188—191°/37 mm., *o*-OAlk·C_6H_4·CO_2Me in which Alk = Et, Pr^{α}, b.p. 165—170°/40 mm., Bu^{α}, b.p. 184—190°/40 mm., *n*-$C_{12}H_{25}$, b.p. 211—216°/2·5 mm., Pr^{β}, b.p. 182—190°/95 mm., and *iso*-C_5H_{11}, b.p. 184—194°/40 mm., and *m*-OAlk·C_6H_4·CO_2Et in which Alk = Et, b.p. 171—181°/37 mm., Bu^{α}, b.p. 192—198°/38 mm., and *n*-amyl, b.p. 200—206°/30 mm. NaOH–EtOH then gives *p*-OAlk·C_6H_4·CO_2H in which Alk = Pr^{α}, m.p. 139—142° (b.p. 175—178°/30 mm.; these and other figures in parentheses below refer to derived acid chlorides, prepared by PCl_5), Bu^{α}, m.p. 145·5—147° (b.p. 191—193°/33 mm.), *n*-amyl, m.p. 118—121° (b.p. 198—200°/30 mm.), *n*-hexyl, m.p. 105—106° (b.p. 213—214°/30 mm.), *n*-C_7H_{15}, m.p. 90—92° (b.p. 226—227°/30 mm.), *n*-$C_{12}H_{25}$, m.p. 137° (b.p. 251—261°/2·5 mm.), Pr^{β}, m.p. 163—165° (b.p. 177—181°/47 mm.), Bu^{β}, m.p. 137—138° (b.p. 181—187°/30 mm.), β-octyl, m.p. 58—62°, b.p. 203—213°/2 mm. (b.p. 224—229°/40 mm.), and allyl, m.p. 160—162° [(prep. by PCl_5), b.p. 186—191°/45 mm.], *o*-acids in which Alk = Et (b.p. 172—184°/50 mm.), Pr^{α}, b.p. 205—207°/40 mm. (b.p. 182—192°/50 mm.), Bu^{α}, b.p. 211—221°/35 mm. (b.p. 189—205°/47 mm.), *n*-$C_{12}H_{25}$, m.p. 43—47°, b.p. 234—242°/2·5 mm. (b.p. 202—212°/3 mm.), Pr^{β}, b.p. 216—227°/93 mm. (b.p. 174—189°/47 mm.), and *iso*amyl, b.p. 239—246°/95 mm. (b.p. 200—213°/50 mm.), and *m*-acids in which Alk = Et, m.p. 131—135° (b.p. 150—159°/30 mm.), Bu^{α}, m.p. 59—61° (b.p. 153—163°/4 mm.), and *n*-amyl, m.p. 70—71° (b.p. 186—189°/28 mm.). *p*-OMe·C_6H_4·COCl and *p*-OEt·C_6H_4·COCl have b.p. 161—168°/38 mm. and 170—171°/35 mm., respectively. OH·$[CH_2]_2$·NH_2, AlkBr, and conc. aq. KOH, sometimes best + dioxan, at 50—60° give β-*N*-ethyl- (35%), b.p. 164—169°, -*n*-propyl-, b.p. 178—185°, -*n*-butyl-, b.p. 195—205°, -*n*-amyl-, b.p. 215—220°, -n-*heptyl*-, b.p. 248—251°, -n-*dodecyl*- (prep. at 102° or 140°), b.p. 188—198°/4·5 mm., -iso*propyl*-, b.p. 172—174°, -*iso*butyl-, b.p. 185—189°/43 mm., and -allyl-aminoethyl alcohol, b.p. 89—94°/3·5 mm. The OH-amine hydrochloride and acid chloride at 100° give β-n-*butylaminoethyl* p-*methoxy*-, m.p. 127·5—129°, p-*ethoxy*-, m.p. 138—140°, p-n-*propoxy*-, m.p. 136—138°, p-n-*butoxy*-, m.p. 128—130°, p-n-*amyloxy*-, m.p. 124—126°, p-*hexyloxy*-, m.p. 120—123°, p-n-*heptyloxy*-, m.p. 129·5—130·5°, p-n-*dodecyloxy*-, m.p. 142—143°, p-iso*propoxy*-, m.p. 118—120°, p-iso*butoxy*-, m.p. 150—152°, o-n-*propoxy*-, m.p. 135—138°, o-n-*butoxy*-, m.p. 85·5—87°, o-n-*dodecyloxy*-, m.p. 97—99°, and m-n-*butoxy-benzoate hydrochloride*, m.p. 109—110°, β-*ethyl*-, m.p. 135—136°, β-n-*propyl*-, m.p. 110·5—111·5°, β-n-*amyl*-, m.p. 123—125°, β-iso*propyl*-, m.p. 168—170°, β-iso*butyl*-, m.p. 171·5—172·5°, and β-*allyl-aminoethyl* p-n-*butoxy*-, m.p. 94—97°, β-*ethylaminoethyl* p-n-*hexyloxy*-, m.p. 128—129°, β-iso*propyl*-, m.p. 107—109°, and β-iso*butyl-aminoethyl* o-n-*butoxy*-, m.p. 76—77°, *-benzoate hydrochloride*, some of which have high local anæsthetic action. β-n-, m.p. 123·5—126°, and β-iso-*Butylaminoethyl* o-*butylthiolbenzoate hydrochloride* (similarly prepared), m.p. 83—84°, are irritant and weak anæsthetics. R. S. C.

Preparation of *m*-hydroxybenzoic acid. H. E. Ungnade and A. S. Henick (*J. Amer. Chem. Soc.*, 1942, **64**, 1737—1738).—Diazotisation of *m*-NH_2·C_6H_4·CO_2Me, f.p. 37°, b.p. 152—153°/11 mm. (*Ac* derivative, m.p. 136—137°) (from the NO_2-ester by H_2–Raney Ni in

EtOAc at 50 lb.), in H_2SO_4 at 0° and finally boiling in aq. H_2SO_4–Na_2SO_4 is the best method (~80%) of preparing *m*-OH·C_6H_4·CO_2H. R. S. C.

Structures of the mono- and di-bromoveratric acids. L. C. Raiford and R. P. Perry (*J. Org. Chem.*, 1942, **7**, 354—361).—Veratraldehyde is best obtained by dissolving vanillin in warm MeOH and adding alkali and Me_2SO_4; the process can be extended to substituted vanillins, thus giving 2-, m.p. 69—70°, 5-, m.p. 48—49°, and 6-*chloro*-, m.p. 140—141°, 2-, m.p. 84—85°, 5-, m.p. 59—60°, and 6-*bromo*-, m.p. 145—146°, and 5-*iodo*-, m.p. 72—73°, *-veratraldehyde*. Oxidation of the related aldehydes affords 2-, m.p. 205—206°, 5-, m.p. 192—193°, and 6-, m.p. 184—185°, *-bromoveratric acid*. The structures of the Br_2-acids are established as follows. 5-Bromo-6-nitroveratraldehyde (**I**), m.p. 139—140° (cf. Jones *et al.*, *J.C.S.*, 1917, **111**, 923) (*nitroguanylhydrazone*, m.p. 243—244°; *oxime*, m.p. 130—131°; 5-*bromo*-6-*nitro*-3 : 4-*dimethoxycinnamic acid*, m.p. 239—240°), is oxidised ($KMnO_4$) to 5-*bromo*-6-*nitroveratric acid* (**II**), m.p. 203—204° (*acid chloride*, m.p. 110—111°). Reduction ($FeSO_4$–NH_3) of (**I**) and (**II**) yields respectively 5-*bromo*-6-*amino-veratraldehyde*, softens at ~150°, m.p. 162—165°, and *-veratric acid* (**III**), m.p. 173—175°. (**III**) affords (Sandmeyer) 5 : 6-*dibromoveratric acid* (**IV**), m.p. 186—187°, also obtained by oxidising ($KMnO_4$) dibromomethyleugenol. 5-Bromo-2-nitrovanillin (Raiford *et al.*, A., 1928, 1246), aq. $NaHCO_3$, and Me_2SO_4 at ~85° give 5-*bromo*-2-*nitroveratraldehyde*, m.p. 60—70° (*nitroguanylhydrazone*, m.p. 219—220°), oxidised to 5-*bromo*-2-*nitroveratric acid*, m.p. 145—146°. 2 : 5-Dibromovanillin is methylated to 2 : 5-dibromoveratraldehyde, m.p. 145—147°, oxidised to 2 : 5-*dibromoveratric acid* (**V**), m.p. 186—187°. 6-*Bromo*-2-*aminoveratraldehyde*, m.p. 101° (obtained by reduction of the 2-NO_2-compound), yields 2 : 6-dibromoveratraldehyde, m.p. 136—137°, which is oxidised to 2 : 6-*dibromoveratric acid*, m.p. 122—123°. The (**V**) of Boyen (cf. A., 1888, 680) is (**IV**). H. W.

***N*-Substituted piperonylamides.** S. I. Gertler and H. L. Haller (*J. Amer. Chem. Soc.*, 1942, **64**, 1741).—*Piperonyl-anilide*, m.p. 146—147°, -o-, m.p. 107—108°, and -p-*chloroanilide*, m.p. 206·5—207·5°, -o-, m.p. 137·5—138·5°, -m-, m.p. 121—122°, and -p-*toluidide*, m.p. 149—149·5°, *-α-*, m.p. 192·5—193°, and *-β-naphthalide*, m.p. 156·5—157·5°, *-benzylamide*, m.p. 126·5—127·5°, and -cyclo*hexylamide*, m.p. 167·5—168·5°, are prepared from NH_2R (slightly >2 mols.) and the acid chloride (1 mol.) in boiling C_6H_6. M.p. are corr. R. S. C.

Indian lichens. V. Occurrence of active montagnetol in *Rocella montagnei*. V. S. Rao and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **15, A**, 429—431; cf. A., 1942, II, 265).—d-*Montagnetol*, m.p. 135—136°, $[\alpha]_D$ +16·2° in H_2O, is isolated from *R. montagnei*; in boiling H_2O (3 hr.) it gives *r*-montagnetol, m.p. 155—156° (*loc. cit.*). It is probable that some racemisation of montagnetol occurs in the plant. A. T. P.

Indian lichens. VI. Constitution of erythrin. V. S. Rao and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **16, A**, 23—28; cf. A., 1942, II, 195).—Erythrin (**I**) is erythrityl lecanorate; this agrees with the occurrence of lecanoric acid with (**I**) and montagnetol (*loc. cit.*) in the lichens. (**I**) and CH_2N_2–Et_2O–MeOH give *trimethylerythrin*, $C_{23}H_{28}O_{10}$, m.p. 110—112° (glass), 118—120° (liquid), converted by MeOH–KOH at 55° into 4 : 6 : 2 : 1-$(OMe)_2C_6H_2Me$·CO_2Me and 6 : 2 : 4 : 1-OMe·$C_6H_2Me(OH)$·CO_2Me. Careful decomp. of (**I**) with boiling H_2O affords *d*-montagnetol, m.p. 136°, but further treatment gives *r*-montagnetol, m.p. 156—157°, identical with picroerythrin. A. T. P.

Naphtol AS series. VI. Synthetic experiments. III. Synthesis of "naphthols" with paraffin chains. R. V. Bhat, S. R. Ramachandran, and K. Venkataraman (*J. Soc. Dyers and Col.*, 1942, **58**, 203—206; cf. A., 1942, II, 312).—2-Hydroxy-3-naphth-*m*-aminoanilide (**I**) and C_7H_{15}·COCl or C_9H_{19}·COCl in dioxan at 100° (bath) give the m-*octoyl*, m.p. >350°, or m-*decoyl* derivative, m.p. 181—182°, respectively. *o*-NO_2·C_6H_4·NH_2 and $C_{11}H_{23}$·COCl in C_5H_5N at room temp. afford *dodec*-o-*nitroanilide*, m.p. 54°, reduced (Fe–aq. AcOH) to the -o-*aminoanilide*, m.p. 89—90°, whence by 2 : 3-OH·$C_{10}H_6$·COCl in dry solvent naphtha at 150° (bath) 2-*hydroxy*-3-*naphth*-o-*dodecamidoanilide*, m.p. 164—165°. Also prepared are *dodec*-m-*nitro*-, m.p. 61°, and -m-*amino-anilide*, m.p. 96—97°; 2-*hydroxy*-3-*naphth*-m-*dodec*-, m.p. 206—207° [also obtained from (**I**) and $C_{11}H_{23}$·COCl in dioxan], -m-*myrist*-, m.p. 206—207°, -m-*palmit*-, m.p. 191—192°, -m-*stear*-, m.p. 196—197°, and -m-*ole-amidoanilide*, m.p. 184—185°; *dodec*-, m.p. 110°, *myrist*-, m.p. 113—114°, *palmit*-, m.p. 115—116°, and *stear*-p-*aminoanilide*, m.p. 116—117°; 2-*hydroxy*-3-*naphth*-p-*dodec*-, m.p. 244—245°, -p-*myrist*-, m.p. 233—234°, -p-*palmit*-, m.p. 232—233°, and -p-*stear-amidoanilide*, m.p. 239—240°. Dyeings from the *p*-substituted "naphthols" are characterised by depth of shade, brilliance, and excellent fastness to rubbing, kier-boiling, and light. The relatively weak dyeings from the *o*- and *m*-compounds had only moderate fastness properties. A. T. P.

Lactones related to the cardiac aglycones. VIII. β-Substituted $\Delta^{\alpha\beta}$-butenolides of the naphthalene and indene series. W. S. Knowles, J. A. Kuch, and R. C. Elderfield (*J. Org. Chem.*, 1942, **7**, 374—382). —6 : 2-OMe·$C_{10}H_6$·MgBr and OMe·CH_2·CN give 6-*methoxy*-2-*naphthyl OMe·CH₂ ketone* (**I**), m.p. 97—98·5°, 2-$C_{10}H_7$·OMe, and a *substance*, m.p. 145—146°. (**I**) is transformed by Zn and CH_2Br·CO_2Et into *Et β-hydroxy-β-6-methoxy-2-naphthyl-β-methoxymethylpropionate*, m.p. 53·5—54·5°, which with HBr in AcOH at 130—140° or 48% HBr–AcOH at 100° affords *β-6-methoxy-2-naphthyl-*$\Delta^{\alpha\beta}$*-butenolide* (**II**), m.p. 152—153°. 6 : 2-OAc·$C_{10}H_6$·CO_2H, m.p. 222—224°, is converted ($SOCl_2$) into the chloride, m.p. 120—121°, and thence into the CHN_2 ketone, m.p. 118·5—120°, OAc·CH_2 ketone, m.p. 115—117°, and *β-6-hydroxy-2-naphthyl-*$\Delta^{\alpha\beta}$*-butenolide*, m.p. 236—238° (decomp.), transformed by CH_2N_2 into (**II**). 2-$C_{10}H_7$·CO_2H is slowly hydrogenated to a mixture of decahydro-2-naphthoic acids, m.p. 70—79°, in presence of PtO_2–AcOH; a similar mixture, m.p. 65—78°, is more conveniently obtained by hydrogenating (Raney Ni in NaOH) and then hydrolysing 2-$C_{10}H_7$·CO_2Et. This is converted as usual into *decahydro-2-naphthyl OAc·CH₂ ketone*, b.p. 108—130°/0·2 mm., and thence into a mixture of stereoisomeric *β-decahydro-2-naphthyl-*$\Delta^{\alpha\beta}$*-butenolides*, b.p. 100—118°/10^{-4} mm. Indene-1-carboxylic acid (**III**), m.p. 159·5—161°, best obtained by carbonating a solution of crude indene and Na in dioxan containing a little C_5H_5N, is transformed ($SOCl_2$ in C_6H_6 at room temp.) into the chloride, m.p. 74—76°, which with CH_2N_2 in Et_2O at −5° gives a *compound*, $C_{12}H_{10}ON_4$, m.p. 111—113° (decomp.), probably a pyrazoline. Mg indenyl bromide and OMe·CH_2·CN give an unstable, obscure *compound*, m.p. 49—50°. Na indenyl and OMe·CH_2·CN give only indene. (**III**) is readily hydrogenated (Pd-black in AcOH) to indane-1-carboxylic acid (**IV**), m.p. 57—58°, converted through the chloride (whence the *amide*, m.p. 162—163°) into 1-*indanyl OAc·CH₂ ketone*, b.p. 135°/0·5 mm. This with CH_2Br·CO_2Et and Zn affords a product giving a strong Legal test but from which a butenolide could not be isolated. *Hydrindane-1-carboxylic acid*, m.p. 94—96°, prepared by hydrogenating (PtO_2 in AcOH) (**III**) or (**IV**) gives a chloride (whence the *amide*, m.p. 204·5—207°), CH_2N_2 ketone, and 1-*hydrindanyl OAc·CH₂ ketone*, m.p. 59—61°, which yields *β-1-hydrindanyl-*$\Delta^{\alpha\beta}$*-butenolide*, m.p. 94—95°. M.p. and b.p. are corr. None of the butenolides was active when tested in frogs. H. W.

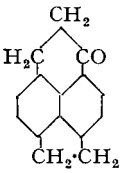
Condensation of primary di- and poly-amines with phthalic anhydride in acetic acid. G. Wanag [with G. Wunderlich and A. Veinbergs] (*Ber.*, 1942, **75**, [*B*], 719—725; cf. A., 1939, II, 506).—The use of *o*-$C_6H_4(CO)_2O$ (**I**) for the characterisation of aromatic di- and poly-amines is generally less satisfactory than for monoamines. In some cases sparingly sol. additive compounds result which pass into phthalyl derivatives with greater or less difficulty whilst in other instances other products or mixtures are formed. The m.p. of the derivatives are frequently inconveniently high. In some cases the products are so sparingly sol. that purification is difficult. Aliphatic amines react normally, giving compounds with accurately determinable m.p., but the differences of m.p. among the simpler members are small. For each NH_2 group in the mol., 1·5—2 mols. of (**I**) and 30—60 mols. of AcOH per mol. of amine are used. NN′-o-, m.p. 293°, NN′-m-, m.p. 318°, and NN′-p-, m.p. 357°, *-phenylene*-, NN′-o-, m.p. 265°, NN′-m-, m.p. 233°, NN′-p-, m.p. 322°, and NN′-symm., m.p. 274°, *-toluylene-diphthalimide* are obtained in normal reaction. Normal *diphthalyl* derivatives, m.p. 276°, 328°, 308°, 428°, 199°, and decomp. 320° after softening at 260°, are derived from 2 : 4′- and 2 : 2′-$(C_6H_4$·$NH_2)_2$, $CH_2(C_6H_4$·NH_2-*p*$)_2$, $(:CH·C_6H_4·NH_2$-*p*$)_2$, $(:C·C_6H_4·NH_2$-*p*$)_2$, and naphthidine. 1 : 4-, 1 : 5-, and 2 : 7-$C_{10}H_6(NH_2)_2$ give normal *diphthalyl* compounds, m.p. 402°, 442—444° (decomp.), and 298°, respectively. 1 : 8-$C_{10}H_6(NH_2)_2$ gives the red *phthaloperin-10-one*, m.p. 232°, whereas 1 : 2-$C_{10}H_6(NH_2)_2$ gives a mixture of compounds. 1 : 3 : 5-*Triphthalimidobenzene*, decomp. >420°, and 2 : 4 : 6-*triphthalimidotoluene*, m.p. 358° (decomp.), are obtained normally. Leucofuchsin affords 4 : 4′ : 4″-*triphthalimido-3-methyltriphenylmethane*, m.p. 329°, and fuchsin in presence of NaOAc gives 4 : 4′ : 4″-*triphthalimido-3-methyltriphenylcarbinol*, m.p. 323°. 4 : 6 : 4′ : 6′-*Tetraphthalimidodi-m-tolylmethane* has m.p. ~370° (decomp.). *Diphthalimidomethane*, m.p. 232°, *αβ-diphthalimidoethane*, m.p. 236°, *αγ-*, m.p. 198°, and *αβ-*, m.p. 232°, *-diphthalimidopropane*, *αδ-diphthalimidobutane*, m.p. 227°, and *αε-diphthalimidopentane*, m.p. 188°, are described. H. W.

Diene syntheses with derivatives of α-amino-$\Delta^{\alpha\gamma}$**-butadiene.** W. Langenbeck, O. Gödde, L. Weschky, and R. Schaller (*Ber.*, 1942, **75**, [*B*], 232—236).—Addition of NEt_2·CH:CH·CH:CH_2 (**I**) to CH_2:CH·CHO in Et_2O gives 2-*diethylamino*-1 : 2 : 5 : 6-*tetrahydrobenzaldehyde*, b.p. 90—93°/3 mm., which gradually decomposes when kept and is converted by 5% HCl into 2 : 3-dihydrobenzaldehyde, b.p. 77—79°/20 mm. [*semicarbazone*, m.p. 182°; oxime, m.p. 39° (lit. 44°)], oxidised by Ag_2O in alkaline solution to the unstable dihydrobenzoic acid (dibromide, m.p. 166—167°). CHMe:CH·CHO and (**I**) in Et_2O slowly yield (after hydrolysis) dihydro-*o*-tolualdehyde, b.p. 88—90°/21 mm. (semicarbazone, m.p. 201°), in 16% yield. *p*-O:C_6H_4:O and piperidinobutadiene afford unchanged material, much quinol, and a small amount of α-naphthaquinone; this is transformed by (**I**) into anthraquinone. Naphthazarin and (**I**) give quinizarin. H. W.

Diene syntheses with oxyprenes. I. 4-Methoxy-, 4-ethoxy-, and 4-methoxy-2-methyl-Δ^3**-tetrahydrobenzaldehyde.** H. Fiesselmann

(*Ber.*, 1942, **75**, [*B*], 881—891).—4-*Ethoxy*-Δ^3-*tetrahydrobenzaldehyde* (**I**), b.p. 104—105°/13 mm. (*semicarbazone*, m.p. 163°), is obtained in 51% yield from CH_2:CH·C(OEt):CH_2 and CH_2:CH·CHO in presence of quinol (**II**) at 100—110°, in 68% yield from the reactants in boiling C_6H_6 (20—24 hr.), and in 74% yield in C_6H_6 containing (**II**) at 100° or at 160°. 4-*Methoxy*-Δ^3-*tetrahydrobenzaldehyde* (**III**), b.p. 94—95°/13 mm., gives a *semicarbazone*, m.p. 151°, *dimedon* compound, $C_{24}H_{34}O_5$, m.p. 142°, and 2 : 4-*dinitrophenylhydrazone*, m.p. 163°. CH_2:CH·C(OMe):CH_2 and CHMe:CH·CHO in C_6H_6 at 160° yield 4-methoxy-2-methyl-Δ^3-tetrahydrobenzaldehyde (**IV**), b.p. 102°/12 mm. (*dimedon* compound, m.p. 163°; 2 : 4-*dinitrophenylhydrazone*, m.p. 125°). Δ^3-Tetrahydrobenzaldehyde (**V**) is oxidised by Ag_2O to Δ^3-tetrahydrobenzoic acid (**VI**), b.p. 125—126°/13 mm.; similarly (**I**) and (**IV**) give respectively *cyclo*hexanone-4-carboxylic acid and 3-methyl*cyclo*hexanone-4-carboxylic acid, b.p. 81°/0·03 mm. (*semicarbazone*, m.p. 205°). The oxime, b.p. 106—108°/14 mm., of (**V**) and Ac_2O give Δ^3-tetrahydrobenzonitrile, b.p. 74°/12 mm., hydrolysed to (**VI**). Hydrogenation (PtO_2 in abs. EtOH or EtOAc) of (**III**) yields 4-*methoxy*-Δ^3-*tetrahydrobenzyl alcohol*, b.p. 116°/12 mm. (p-*nitrobenzoate*, m.p. 111·5°), converted by 2 : 4-$(NO_2)_2C_6H_3$·NH·NH_2 in dil. H_2SO_4 into 4-*hydroxymethyl*cyclo*hexanone*-2 : 4-*dinitrophenylhydrazone*, m.p. 143°. $Al(OPr^\beta)_3$ in boiling C_6H_6 converts (**V**) into Δ^3-tetrahydrobenzyl alcohol, b.p. 82°/12 mm. (p-*nitrobenzoate*, m.p. 62°). Ac_2O and NaOAc at 180° transform (**V**) into its *enol acetate*, b.p. 91—92°/12 mm. H. W.

***N*-Methylformanilide synthesis of aldehydes.** L. F. Fieser and J. E. Jones (*J. Amer. Chem. Soc.*, 1942, **64**, 1666—1669).—Aldehydes are obtained by NPhMe·CHO–$POCl_3$ from aromatic hydrocarbons having a reactive nuclear position and not too sensitive to $POCl_3$. Thus. 9-methylanthracene at 100° gives 9-*methylanthracene*-10-*aldehyde* (84%), m.p. 171·9—172·6° [*oxime*, m.p. 210° (decomp.); *hydrazone*, m.p. 175·1—175·8°, converted by NaOEt–EtOH at 200—210° into 9 : 10-dimethylanthracene]. In *o*-$C_6H_4Cl_2$ 3 : 4-benzpyrene gives 90% of the 5-aldehyde, 1 : 2-benzanthracene gives 64% of the 10-aldehyde, (**III**) (below) gives a mixture (68%), and 3-methylpyrene gives a mixture (73%), yielding a (? homogeneous) *semicarbazone*, m.p. 138—140°, but 1 : 2 : 5 : 6-dibenzanthracene does not react. Hydrindene, 1-$C_{10}H_7Me$, phenanthrene, and chrysene do not react at 20—150°. Acenaphthene (**I**) at 95° and perinaphthane at 25° are too sensitive, yielding tars. At 25° in *o*-$C_6H_4Cl_2$ (6 days), (**I**) gives 3-*acenaphthaldehyde* (**II**) (85%), m.p. 107·4—108°, sublimes at 110°/2 mm. [oxime, m.p. 126·8—127·9° (lit. 126·5°); semicarbazone, m.p. 247·8—248·8° (lit. 234°)], oxidised by 30% H_2O_2 + 10% NaOH in dioxan to the acid and reduced by H_2–PtO_2–$FeCl_2$ in EtOH to 3-*hydroxymethylacenaphthene* (73%), m.p. 153·8—154·8°. With N_2H_4,H_2O (excess) at 200—210° (N_2; 2250 lb.), (**II**) gives 3-*methylacenaphthene* (**III**), m.p. 95·6—95·9° [*picrate*, m.p. 163° (decomp.)], and some azine. With $CH_2(CO_2H)_2$–C_5H_5N at 100°, (**II**) gives β-3-*acenaphthylacrylic* (83%), m.p. 251·3—251·8° (gas) and +$2H_2O$, m.p. indefinite [*Me* ester (**IV**), *forms*, m.p. 104·4—105·4° and 73—74°], reduced (2% Na–Hg; 0·5N-NaOH) to β-3-*acenaphthylpropionic acid* (93%), m.p. 191·7—192° [*Me* ester, m.p. 50·7—51·7°, prepared from (**IV**) by H_2–PtO_2–EtOH], which in HF yields 3 : 4-*aceperinaphthan*-7-*one* (**V**) (40%), m.p. 102·6—103·4°, unstable in light [purified by way of the *oxime*, m.p. 245—246° (darkens at 225°); *semicarbazone*, m.p. 268° (vac.; preheated at 260°)]. CrO_3–AcOH–H_2O oxidises (**V**) to 1 : 4 : 5 : 8-$C_{10}H_4(CO_2H)_4$, and Zn–Hg–HCl–AcOH–PhMe gives 3 : 4-*aceperinaphthane* (30%), m.p. 121·4—122° [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 147—148°]. M.p. are corr.


(**V.**)

R. S. C.

Reaction of β-*iso*durylaldehyde cyanohydrin with magnesium phenyl bromide. A. Weissberger and D. B. Glass (*J. Amer. Chem. Soc.*, 1942, **64**, 1724—1727).—Acetomesitylene derivatives show enhanced enolisation due to high electron-*d* in the nucleus (as compared with Ph). 2 : 4 : 6 : 1-$C_6H_2Me_3$·CHO [prep. from *s*-$C_6H_3Me_3$ by $Zn(CN)_2$ and HCl; 75% yield] (0·3), b.p. 113—115°/11 mm., in light petroleum with KCN (0·8) and NH_4Cl (0·83 mol.) in H_2O gives α-*hydroxy*-α-*mesitylacetonitrile* (**I**) (91%), m.p. 106—107° (sealed tube), which with MgPhBr–Et_2O etc. gives 2 : 4 : 6-*trimethyldesylamine hydrochloride* (**II**) (55%), m.p. 290—291° (sealed tube). (**I**) reacts with 2 MgMeI, evolving 1 CH_4, and thus gives OMgBr·CHAr·CR:N·MgBr; formation of NH_2, as in (**II**), occurs after hydrolysis. (**II**) shows 3 active H and no addition. 2 : 4 : 6 : 1-$C_6H_2Me_3$·CO·CH_2Ph, b.p. 136—137°/0·5 mm., and OBu·NO in Et_2O–HCl give the :N·OH-compound, m.p. 156—156·5°, reduced by $SnCl_2$–conc. HCl–EtOH to (**II**). Ac_2O–C_5H_5N at 100° converts (**II**) first into β-*acetamido*-α-*hydroxy*-2 : 4 : 6-*trimethylstilbene* [*acetyl*-2 : 4 : 6-*trimethyldesylamine*] (**III**), m.p. 174·5—175° (2 active H; no addition of MgMeI), and then β-*diacetamido*-α-*acetoxy*-2 : 4 : 6-*trimethylstilbene* (**IV**), m.p. 125—126° (no active H; adds 4 MgMeI). Boiling conc. HCl–EtOH hydrolyses (**IV**) to (**III**) and then slowly to (**II**). Desylamine (**V**) gives similarly *Ac*$_1$, m.p. 135—136° (1 active H; adds 1 MgMeI), and *Ac*$_3$ derivatives, m.p. 130—131°. With HCl–EtOH–H_2O–N_2 at 95° (20 hr.) and 130° (24 hr.), (**V**) gives 40 and 100%, respectively, of benzoin; at 95° (**II**) is unaffected and at 130° gives 20% of 2 : 4 : 6-trimethyl-benzoin and -benzil. R. S. C.

Reduction of the stereoisomeric δ-enol methyl ethers of αδ-dimesitylbutane-αβδ-trione. R. E. Lutz and D. H. Terry (*J. Org. Chem.*, 1942, **7**, 320—325).—*cis*-δ-Methoxy-αδ-dimesityl-Δ^γ-butene-αβ-dione (**I**) is obtained in 58% yield (with 6·5% of αδ-dimesityl-β-methyl-Δ^β-buten-γ-ol-αδ-dione) by the action of MeI on the Ag salt of dimesitylbutanetrione enol (**II**) in dry Pr^β_2O or (67%) by the action of aq. $AgNO_3$ on a solution of (**II**) in MeOH containing NaOMe. (**I**) is converted by acid, base, heat, or sunlight into the *trans*-isomeride (**III**). (**I**) and (**III**) are easily hydrolysed by acids to (**II**); the reagents used would first convert (**I**) into (**III**). Attempts to obtain individual oximes lead only to the oxime, m.p. 166·5—167°, of (**II**). (**I**) and (**III**) absorb H_2 giving individual and persistent enediols which are readily oxidised to the parent compounds and undergo rearrangement to cis- (**IV**), m.p. 145—146° [accompanied by a small amount of a compound (**V**), m.p. 135—136°, also obtained from CH_2N_2 and δ-hydroxy-αδ-dimesitylbutane-αγ-dione enol], and trans-, m.p. 120°, -α-*hydroxy*-δ-*methoxy*-αδ-*dimesityl*-Δ^γ-*buten*-β-*one* (**VI**). (**IV**) is converted almost quantitatively into (**VI**) by exposure to sunlight of its solution in MeOH or $CHCl_3$ containing I. Hydrolysis of (**IV**) by HCl in AcOH or MeOH gives unidentified compounds, m.p. 179·5—180° or 91°, respectively. NH_2OH and NaOAc in boiling dil. EtOH leave (**IV**) largely unchanged but yield a small proportion of (**V**), and are without action on (**VI**), which is converted by air at 200° into (**III**). Reduction of (**VI**) by red P and I in AcOH gives an unidentified compound, m.p. 164—168°, and αδ-dimesitylbutane-αγ-dione enol, also obtained with an unexamined substance, m.p. 227—229°, by reduction of (**VI**) with Zn dust and HCl in aq. EtOH. (**VI**) with Sn and conc. HCl in AcOH affords αδ-dimesitylbutan-β-one, m.p. 118·5—119·5°; these reductions involve demethylation. (**IV**) or (**VI**) with PCl_5 in $CHCl_3$ at 15° and then at 40° yields α-*chloro*-δ-*methoxy*-αδ-*dimesityl*-Δ^γ-*buten*-β-*one* (**VII**), m.p. 138·5—139°. Catalytic reduction (PtO_2 in EtOH) of (**VII**) leads to δ-methoxy-αδ-dimesityl-Δ^γ-buten-β-one. (**VII**) is hydrolysed by Ag_2O in MeOH to (**VI**) and by KOH–aq. MeOH to (**III**). Boiling aq. C_5H_5N has no action on (**VII**). There is no rigorous proof of the abs. configuration of any one of the above compounds from which the configurations of the others would follow. The formulæ are proposed on the hypothesis that the most stable type is that in which the bulkier groups, mesityl and mesitylglyoxyl, are *trans* with respect to each other. There appears to be no consistent relation between the chelate enol form and the configuration of the products of methylation by CH_2N_2. H. W.

Tertiary bases and betaines from piperitone oxide. H. Rupe and M. Refardt (*Helv. Chim. Acta*, 1942, **25**, 836—859; cf. A., 1939, II, 71).—Interaction of piperitone oxide (**I**) with 20% EtOH–$NHMe_2$ at 100—110° gives 2-*dimethylamino*-3-*methyl*-6-iso*propyl*-Δ^2-(~44%) (**II**), and -Δ^3-cyclo*hexenone* (~35%) (**III**), and a base (~5%) (**IV**), $C_{12}H_{21}ON$, separated from one another mainly through their salts. (**I**) is obtained by the action of NaOH and H_2O_2 on piperitone in Pr^αOH but can be separated from unchanged material only with great difficulty; its properties vary from specimen to specimen in an unexplained manner. It gives a *semicarbazone*, two forms, m.p. 182—183° and 197°, and an *oxime*, m.p. 101°, from which it cannot be satisfactorily regenerated. (**II**), b.p. 110—111°/11 mm., $[\alpha]_D^{20}$ −5·63°, rapidly becomes yellow when exposed to air. It does not contain active H (Zerevitinov). It gives a *perchlorate*, m.p. 140—141°, $[\alpha]_D^{20}$ −6·35° in H_2O, *picrate*, m.p. 144—145°, *semicarbazone*, m.p. 206—208°, and *methiodide*, m.p. 115—116°, but a hydrochloride, hydrobromide, tartrate, oxalate, oxime, Ac or Bz derivative could not be prepared. It does not add (:CH·CO)$_2$O. It reacts with 2 mols. of N_2H_4,H_2O giving a *dihydrazine* derivative, m.p. 68°, thus establishing the presence of a double linking in the αβ-position to :CO. It is transformed by MgEtBr into 2-*dimethylamino*-3-*methyl*-1-*ethyl*-6-iso*propyl*-Δ^2-cyclo*hexenol*, b.p. 124—127°/10 mm. (*perchlorate*, m.p. 186—187°; *hydrobromide*, m.p. 133—134°), which with CH_2Br·CO_2Et affords the *betaine ester hydrobromide*, $C_{18}H_{34}O_3NBr$, m.p. 204—205°. (**II**) is hydrogenated (Rupe Ni in aq. EtOH) to a mixture of 2-*dimethylamino*-3-*methyl*-6-iso*propyl*-Δ^2-cyclo*hexenol*, m.p. 139—140°, and -cyclo*hexanol*, b.p. 120°/11 mm. (*picrate*, m.p. 151—153°). (**II**) and CH_2Br·CO_2Et at room temp. and preferably under the influence of light slowly yield the *betaine ester hydrobromide*, $C_{16}H_{28}O_3NBr$, m.p. 208—209°, from which the free betaine could not be obtained. Under other conditions the change proceeds with difficulty. At 120—150° in a sealed tube a small amount of CO_2H·CH_2·NMe_3Br is produced with an unexplained acidic compound, m.p. 310°. (**II**) does not appear to react with CH_2Cl·CO_2Et and gives neutral crystals, m.p. 124—126°, with CH_2I·CO_2Et. (**III**), b.p. 132—133°/12 mm., $[\alpha]_D^{20}$ +0·65°, is a colourless liquid which rapidly becomes yellow when exposed to air. It is characterised by a *hydrobromide*, m.p. 219—220°, *hydrochloride*, (+0·5H_2O), m.p. 208—209°, *picrate*, m.p. 181—182°, *methiodide*, m.p. 217°, *hydrazone*, m.p. 39—41° (probably accompanied by the corresponding *azine*), *semicarbazone*, m.p. 204—205°, and *oxime* (+1H_2O), m.p. 93—95°. (**III**) contains OH (Zerevitinov) and although it usually reacts as a ketone it behaves as enol towards Grignard's reagents but does not yield an Ac or Bz derivative. Hydrogenation of (**III**) proceeds less readily than that of (**II**) and in presence of Ni leads to a solid *base* con-

sidered to be the H_2-substance, m.p. 81—83°, and a liquid *compound*, b.p. 125—128°/12·5 mm., in which saturation of the Δ^3-double linking has probably occurred; CO of both products is reduced since the compounds fail to react with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ and contain active H (Zerevitinov); they both give the same *hydrochloride*, m.p. 199—200°. (**III**) and $CH_2Br{\cdot}CO_2Et$ at room temp. readily afford the *hydrobromide*, m.p. 210—211°, of the betaine Et ester, from which the free *betaine*, m.p. 239—241°, is obtained by means of Ag_2O. (**IV**), $[\alpha]_D^{20}$ +1·53°, appears to be isomeric with (**II**) and (**III**) and much more closely allied to (**III**) than to (**II**), It gives a *hydrochloride* (+0·5H_2O), m.p. 202—204°, *perchlorate*, m.p. 186—188°, *oxime* (non-cryst.), *semicarbazone*, m.p. 205—206°, and (with N_2H_4,H_2O) a *compound*, $C_{24}H_{42}N_4$. It contains active H (Zerevitinov) but does not give an Ac or Bz derivative or a Me ether. It appears to be a keto-enolic form. With $CH_2Br{\cdot}CO_2Et$ it yields the corresponding *betaine ester hydrobromide*, m.p. 209—211°, converted by Tl_2CO_3 but not by Ag_2O into the free *betaine*, m.p. 248°. (**IV**) is hydrogenated to a *base*, $C_{12}H_{23}ON$, m.p. 124—126°.

H. W.

Condensation of 2-methylene*cyclo*hexanone with malonic ester. C. Mannich and W. Koch (*Ber.*, 1942, **75**, [*B*], 803—805).—The catalytic action of NaOEt at room temp. during several days on a mixture of 2-dimethylaminomethyl*cyclo*hexanone and $CH_2(CO_2Et)_2$ gives $NHMe_2$ and Et_2 2-keto*cyclo*hexylmethylmalonate (**I**), b.p. 195—197°/15 mm. (*semicarbazone*, m.p. 108°), the intermediate formation of 2-methylene*cyclo*hexanone being postulated. (**I**) is hydrolysed and decarboxylated to β-2-*keto*cyclo*hexylpropionic acid* (**II**), m.p. 65° (*semicarbazone*, m.p. 186°), transformed by boiling Ac_2O into *hexahydrocoumarin*, b.p. 141—142°/15 mm., converted by long boiling with aq. $COMe_2$ into (**II**) and by NH_3–EtOH into the *amide*, m.p. 160°, of (**II**).

H. W.

Migration of acyl groups in the orcinol series. F. Mauthner (*J. pr. Chem.*, 1942, [ii], **160**, 38—40; cf. A., 1934, 656; 1937, II, 98).—1 : 3 : 5-$C_6H_3Me(OAc)_2$ and $AlCl_3$–$PhNO_2$ at room temp. yield (mainly) 1 : 3-*diketo*-2 : 4-*diacetyl*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydrobenzene*, m.p. 93—94° (*mono*-p-*nitrophenylhydrazone*, m.p. 225—226°), a little 3 : 5 : 1 : 4-$(OH)_2C_6H_2Me{\cdot}COMe$ (p-*nitrophenylhydrazone*, m.p. 257—258°), and a *substance*, m.p. 55—56°, b.p. 163—164°/12 mm. (no reaction with p-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$).

A. T. P.

Dehalogenation of glycol halohydrins and isomerisation of the corresponding epoxides in the hydrindene and tetrahydronaphthalene series. B. Tchoubar (*Compt. rend.*, 1942, **214**, 117—119).—1 : 2- and 1 : 4-Dihydronaphthalene epoxides (prep. by BzO_2H-oxidation) with $MgBr_2$ in Et_2O, followed by H_2O, yield respectively 2-keto-tetrahydronaphthalene and a mixture of this with aldehydohydrindene. Indene oxide (from the bromohydrin with solid KOH in Et_2O) similarly (or on passing the vapour over infusorial earth at 270—290°) yields 2-indanone, whilst indene bromohydrin gives 1-indanone, also obtained from the iodohydrin with KOH in Et_2O.

A. Li.

New class of odoriferous compounds. Buu-Hoï and P. Cagniant (*Compt. rend.*, 1942, **214**, 115—117).—p-$C_6H_4MeBu^{\gamma}$ with Br and a trace of Fe yields 1 : 4 : 2-$C_6H_3MeBu^{\gamma}Br$, b.p. 121—123°/10—11 mm., which with Mg in Et_2O (+EtBr to start the reaction) followed by $(CH_2)_2O$ at −10° gives 2 : 5 : 1-$C_6H_3MeBu^{\gamma}{\cdot}[CH_2]_2{\cdot}OH$, b.p. 155—160°/10—11 mm. The corresponding bromide, b.p. 154—158°/11 mm., with $CHNa(CO_2Et)_2$ in EtOH yields an ester, b.p. 217—218°/7—8 mm., hydrolysed and decarboxylated to 2 : 5 : 1-$C_6H_3MeBu^{\gamma}{\cdot}[CH_2]_3{\cdot}CO_2H$, b.p. 204—207°/8—9 mm., the chloride ($SOCl_2$), b.p. 175°/10 mm., of which is cyclised ($AlCl_3$ in C_6H_6) to 1-keto-5-methyl-8-*tert.*-butyl-1 : 2 : 3 : 4-tetrahydronaphthalene (**I**), m.p. 78° (semicarbazone, m.p. 223°; *compound*, $C_{31}H_{36}ON_4$, m.p. 232—233°, from p-$NO{\cdot}C_6H_4{\cdot}NMe_2$ in alkali). Similarly 1 : 4 : 3-$C_6H_3MeBu^{\gamma}{\cdot}OMe$ yields (Br in AcOH at ⩾10—15°) 1 : 4 : 6 : 3-$C_6H_2MeBu^{\gamma}Br{\cdot}OMe$, m.p. 108—109°, β-4-methoxy-2-methyl-5-*tert.*-butyl-phenylethyl alcohol, b.p. 170—180°/10—11 mm. (bromide, m.p. 53°), and -γ-phenylbutyric acid, m.p. 53° [from the substituted malonic acid, m.p. 183° (Et_2 ester, b.p. 224—225°/7 mm.)], and 1-keto-7-methoxy-5-methyl-8-*tert.*-butyl-1 : 2 : 3 : 4-tetrahydronaphthalene (**II**), m.p. 57° (semicarbazone, m.p. 227—230°; *compound*, $C_{32}H_{38}ON_4$, m.p. 205—206°, from p-$NO{\cdot}C_6H_4{\cdot}NMe_2$). p-$C_6H_4Bu^{\gamma}{\cdot}CH_2Cl$ yields p-$C_6H_4Bu^{\gamma}{\cdot}[CH_2]_3{\cdot}OH$, b.p. 155—156°/9 mm. (bromide, b.p. 153—154°/9 mm.), substituted malonic acid, m.p. 149° (Et_2 ester, b.p. 218—222°/8—9 mm.), δ-*p-tert.*-butylphenyl-valeric acid, b.p. 205—207°/8 mm., m.p. 72° (chloride, b.p. 180°/9 mm.), and 8-*tert.*-butyl-α-benzosuberone (**III**), m.p. 40° (semicarbazone, m.p. 192—193°; oxime, m.p. 122—123°). (**I**) and (**III**) have an odour of sandalwood, but (**II**) is odourless.

A. Li.

Preparation of 2 : 3 : 5 : 6-tetrabromobenzoquinone. H. H. Hodgson and C. K. Foster (*J.C.S.*, 1942, 583).—4 : 2 : 6 : 1-$NH_2{\cdot}C_6H_2Br_2{\cdot}OH$ is diazotised in dil. H_2SO_4 at 5°; the resulting diazo-oxide with Br–AcOH at 80—100° gives 2 : 3 : 5 : 6-tetrabromobenzoquinone, m.p. 300°.

A. T. P.

Preparation of 4 : 6-dimethoxytoluquinone. A. E. Oxford (*J.C.S.*, 1942, 583).—2 : 6-Dimethoxybenzoquinone (18% excess) and $(AcO)_2$ in AcOH at 80°, then at 100° (added to H_2O and extracted 21 times with light petroleum and twice with CCl_4), give 4 : 6-dimethoxytoluquinone (20% yield), m.p. 125—126°, and a trace of 2 : 6-dimethoxy-3 : 5-dimethylbenzoquinone.

A. T. P.

Synthesis and anti-bacterial properties of alkyl and alkenyl derivatives of 2 : 6-dimethoxybenzoquinone. A. E. Oxford (*J.C.S.*, 1942, 577—578).—2 : 6-Dimethoxybenzoquinone (**I**) (9% excess) and $(Alk{\cdot}CO{\cdot}O)_2$ (**II**) in AcOH at 80—100° (15 to 30 min.) give 2 : 6-*dimethoxy*-3-*ethyl*-, m.p. 59°, -*propyl*-, m.p. 20°, -*isobutyl*-, m.p. 50—51°, and -*propenyl-benzoquinone*, m.p. 84°. (**I**) and (**II**) (7% excess) in AcOH afford 2 : 6-*dimethoxy*-3 : 5-*dimethyl*-, m.p. 134°, and impure -diethyl-benzoquinone (an oil). The reaction failed with di*iso*butyryl and disuccinyl peroxide. None of the quinones is more active against *Staph. aureus* than 4 : 6-dimethoxytoluquinone.

A. T. P.

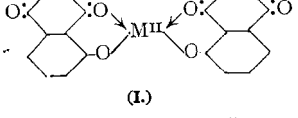
Synthesis of phthiocol and its homologues. Buu-Hoï and P. Cagniant (*Compt. rend.*, 1942, **214**, 87—90).—1-Keto-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (*A*), b.p. 142—143°/9—10 mm. (semicarbazone, m.p. 177°) [from $CH_2Ph{\cdot}COMe$ by treatment with $CH_2Br{\cdot}CO_2Et$ and Zn in C_6H_6, dehydration (P_2O_5 in C_6H_6), hydrogenation (Pt), saponification, and cyclisation ($SOCl_2$ followed by $AlCl_3$)], with p-$NO{\cdot}C_6H_4{\cdot}NMe_2$ (**I**) in aq. EtOH–NaOH yields the 2 : 4-di-(*p*-dimethylaminoanilo)-derivative (an oil), hydrolysed (5% H_2SO_4) to 2-hydroxy-3-methyl-1 : 4-naphthaquinone [phthiocol (**II**)]. Similarly 1-keto-3-ethyl- (*B*) (from $CH_2Ph{\cdot}COEt$), b.p. 148—150°/7 mm. (semicarbazone, m.p. 171—172°), -3-propyl- (*C*) (from $CH_2Ph{\cdot}COPr$), b.p. 160—163°/8—9 mm. (semicarbazone, m.p. 183—185°), -6-methoxy-, and -7-*tert.*-butyl-1 : 2 : 3 : 4-tetrahydronaphthalene, and 1-keto-9-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene with (**I**) yield products, m.p. —, —, 211°, 205°, and 227°, respectively, hydrolysed to 2-hydroxy-3-ethyl-, m.p. 138°, -3-propyl-, m.p. 101°, -6-methoxy-, decomp. 197—200°, and -7-*tert.*-butyl-1 : 4-naphthaquinone, m.p. 110°, and 2-hydroxy-9-methoxy-1 : 4-phenanthrenequinone, m.p. 207—208° (decomp.), respectively. 1-Keto- and 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene with (**I**) yield bisazomethine compounds, m.p. 223° and 238°, respectively, which could not be hydrolysed. 1-Keto-2 : 2-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene and benzosuberone react with (**I**), but do not give the expected products. 1-Keto-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene does not yield (**II**). Physical data of the intermediates in the prep. of (*A*), (*B*), and (*C*) are given.

A. Li.

Synthesis of 3 : 5 : 6(or 7) : 8-tetrahydroxy-2-ethyl-1 : 4-naphthaquinone. K. Wallenfels (*Ber.*, 1942, **75**, [*B*], 785—793).—*m*-$C_6H_4(OH)_2$, $CH_2Ac{\cdot}CO_2Et$, and conc. H_2SO_4 give 7-hydroxy-4-methylcoumarin, the acetate of which is isomerised by $AlCl_3$ at 130—175° and then hydrolysed to 1 : 2 : 6-$C_6H_3Ac(OH)_2$. This is methylated ($NaOH$–Me_2SO_4) to 2 : 1 : 6-$OH{\cdot}C_6H_3Ac{\cdot}OMe$, which is oxidised ($K_2S_2O_8$–aq. NaOH at room temp.) to 2 : 5 : 1 : 6-$(OH)_2C_6H_2Ac{\cdot}OMe$; further methylation (Me_2SO_4–NaOH) affords 2 : 3 : 6-*trimethoxyacetophenone*, b.p. 166°/12 mm., m.p. 42°, reduced (Clemmensen) to 2 : 3 : 6-*trimethoxy*-1-*ethylbenzene* (**I**), b.p. 136—137°/12 mm., m.p. 54°. Gradual addition of a molten mixture of (**I**) and $(CH{\cdot}CO)_2O$ to $AlCl_3$–NaCl at 210° yields 3 : 5 : 8-*trihydroxy*-2-*ethyl*-1 : 4-*naphthaquinone* (**II**), m.p. 185°, with a small proportion of the 3-*Me*$_1$ *ether* (**III**), m.p. 83—84°, also prepared from (**II**) and CH_2N_2 in Et_2O. (**III**) is not hydrolysed by conc. alkali and is remarkably stable to acid. (**II**) and $Pb(OAc)_4$ give a brown ppt. of a Pb salt in C_6H_6 or AcOH whereas (**III**) is converted into 3-methoxy-2-ethyl-1 : 4-5 : 8-naphthadiquinone, reddens with decomp. at 50—60°. It is converted by Ac_2O–conc. H_2SO_4 at room temp. followed by hydrolysis by 25% H_2SO_4 at 100° into 5 : 6 (or 7) : 8-*trihydroxy*-3-*methoxy*-2-*ethyl*-1 : 4-*naphthaquinone* (**IV**), m.p. 158—160°, which has a two-band spectrum similar to that of natural echinochrome *A*, and is very resistant to acid and alkali. (**V**) is converted by CH_2N_2 in Et_2O into the corresponding 3 : 6 (or 7)-*Me*$_2$ *ether*, m.p. 139°, and is demethylated by $AlCl_3$ in $PhNO_2$ at 40° to 3 : 5 : 6(or 7) : 8-*tetrahydroxy*-2-*ethyl*-1 : 4-*naphthaquinone*, m.p. 192°.

H. W.

Preparation and properties of *peri*-hydroxyquinone inner complexes. B. P. Geyer [with G. McP. Smith] (*J. Amer. Chem. Soc.*, 1942, **64**, 1649—1651).—1-Hydroxyanthraquinone and metal acetates in H_2O, MeOH, or EtOH give complexes (**I**) in which M = Co (**II**), Cu (**III**), *Mg*, *Mn*, UO_2, *Ni* (anhyd. and +2H_2O). Similar Cu *complexes* (**IV**) and (**V**) are obtained from 3-nitroalizarin and alizarin 2-acetate. The complexes resemble the phthiocol derivatives in absorption in the bands 370—410 and 470—580 mμ., the nature of the metal having little effect. (**II**), (**III**), (**IV**), and (**V**) have a decreasing chemiluminescent effect with lumimol–H_2O_2, but < have the phthiocol complexes.



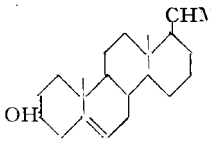
(I.)

R. S. C.

IV.—STEROLS AND STEROID SAPOGENINS.

Structure of fucosterol. H. B. MacPhillamy (*J. Amer. Chem. Soc.*, 1942, **64**, 1732—1733).—Fucosterol (prep. described; new

consts.) has the structure shown, since with O_3 in AcOH it gives MeCHO (33·6% as *p*-nitrophenylhydrazone).



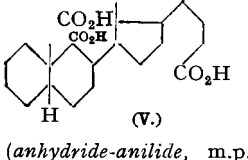
R. S. C.

Marine products. X. Clionasterol. C. A. Kind and W. Bergmann (*J. Org. Chem.*, 1942, **7**, 341—345; cf. A., 1941, II, 289).—Partly an account of work previously abstracted (A., 1942, II, 229). The 2 : 4-*dinitrophenylhydrazone* (**I**), m.p. 227—228°, of Δ^4-clionastenone, $[\alpha]_D^{25}$ +80·2° in $CHCl_3$, has $[\alpha]_D^{25}$ +232° in $CHCl_3$, whilst that of cholestenone has $[\alpha]_D^{25}$ +240·8° in $CHCl_3$; the high $[\alpha]_D$ suggest that these are heterocyclic compounds rather than hydrazones. Clionastane-3 : 5 : 6-triol (*monoacetate*, softens at 235°, m.p. 238°) contains an inert, *tert.* OH since it gives a *diacetate*, m.p. 128—129°, and *dibenzoate*, m.p. 225—228°. It is oxidised (Oppenauer) to *clionasten-5-ol-3* : 6-*dione*, m.p. 189—191°. SeO_2 and boiling Ac_2O followed by hydrolysis convert clionasterol into Δ^4-*clionastene-4* : 5-*diol*, m.p. 231—232°, $[\alpha]_D^{23}$ +8·3° in C_5H_5N (*dibenzoate*, m.p. 206—207)°, oxidised by Brady's solution to (**I**). Clionasteryl acetate is hydrogenated (PtO_2 in AcOH) to poriferastyl acetate, m.p. 139°, $[\alpha]_D^{25}$ +17·8° in $CHCl_3$. The structure of spongella sterol is discussed. H. W.

Dipole moments of bile acids.—See A., 1942, I, 387.

Bile acids and related compounds. XV. 3(α)- and 3(β)-Hydroxy-Δ^{11}-cholenic acid. J. Press and T. Reichstein (*Helv. Chim. Acta*, 1942, **25**, 878—888).—The constitution of 3-keto-Δ^{11}-cholenic acid (**I**) is established. Reduction of the Me ester (**II**) of (**I**) by $Al(OPr^\beta)_3$ and boiling $Pr^\beta OH$, by Na–Hg, or by partial hydrogenation (Raney Ni) gives a mixture separable by digitonin into *Me* 3(α)- (**III**), m.p. 101—102°, $[\alpha]_D^{15}$ +41·5°±2° in MeOH, and *Me* 3(β)- (**IV**), m.p. 109—110°, *-hydroxy-*Δ^{11}*-cholenate*, $[\alpha]_D^{17}$ +38·3°±2° in MeOH, both of which give a yellow colour with $C(NO_2)_4$ and are re-oxidised to (**II**). (**III**) and (**IV**) are converted by Ac_2O in abs. C_5H_5N at room temp. into their respective *acetates* (**V**), m.p. 116—117°, $[\alpha]_D^{14}$ +52·2°±2° in $COMe_2$, and (**VI**), m.p. 147—149°, $[\alpha]_D^{17}$ +28·1°±3° in $COMe_2$, and are hydrolysed to the respective *acids*, m.p. 165—166°, $[\alpha]_D^{11}$ +33·2°±3° in abs. EtOH, and m.p. (hydrated) 77—79°, (anhyd.) ~128°, $[\alpha]_D^{20}$ +27·8°±2° in dioxan. (**V**) and BzO_2H in $CHCl_3$ yield *Me* 11(β) : 12(β)-*oxido*-3(α)-*acetoxycholanate* (**VII**), m.p. 140—142°, $[\alpha]_D^{14}$ +52·8°±2° in $COMe_2$, hydrolysed and subsequently esterified to the 3(α)-*OH-ester*, m.p. 96·9°, $[\alpha]_D^{23}$ +35·7°±2° in $COMe_2$, also obtained from (**III**) and BzO_2H in $CHCl_3$ at 0°. *Me* 11(β) : 12(β)-*oxido*-3(β)-*acetoxycholanate*, m.p. 150—152°, $[\alpha]_D^{16}$ +31·2°±2° in $COMe_2$, similarly affords the 3(β)-*OH-ester*, m.p. 114—115°, $[\alpha]_D^{17}$ +27·1°±2° in $COMe_2$, also derived from (**IV**). Oxidation (CrO_3 in AcOH at room temp.) of either OH-ester leads to *Me* 11(β) : 12(β)-*oxido*-3-*ketocholanate*, m.p. 116—118°, $[\alpha]_D^{22}$ + 32·7°±2° in $COMe_2$. (**VII**) is hydrogenated (Raney Ni) to Me lithocholate and deoxycholate, characterised as their acetates. M.p. are corr. (block). H. W.

Bile acids and related substances. XIII. Δ^{11}-Cholenic acid and 11 : 12-dihydroxycholanic acid. H. B. Althers and T. Reichstein (*Helv. Chim. Acta*, 1942, **25**, 805—821).—Me 12(β)-hydroxycholanate (**I**), m.p. 120—121°, is obtained by heating a mixture of Me 3-keto-12-acetoxycholanate, KOH, EtOH, and N_2H_4,H_2O gradually to 220° and then at 240°, or from the ester, N_2H_4,H_2O, and NaOEt–EtOH at 180°/pressure. The corresponding acid is heated gradually under diminished pressure and finally distilled at 340°/11 mm., thereby giving a small amount of 12(β)-hydroxycholanolactone, m.p. 246—248°, and mainly Δ^{11}-*cholenic acid*, m.p. 133—135°; the *Me* ester (**II**), m.p. 57—59° (60°), $[\alpha]_D^{12}$ +34·1°±2° in $COMe_2$, gives a yellow colour with $C(NO_2)_4$ and is converted by Br in $CHCl_3$ into the *dibromide*, m.p. 102—103°, which regenerates (**II**) when treated with Zn dust and given also some doubly unsaturated ester when boiled with C_5H_5N. (**II**) is hydrogenated (PtO_2 in AcOH) to Me cholanate, m.p. 86—87°, $[\alpha]_D^{11}$ +24·6°±1° in $COMe_2$. Hydroxylation (OsO_4) of (**II**) leads to *Me* 11 : 12-*dihydroxycholanate* (**III**), dimorphous, m.p. 83—85°, $[\alpha]_D^{16}$ +11·3°±1° in MeOH, and m.p. 103—108°, $[\alpha]_D^{15}$ +12·2°±1° in MeOH (*diacetate*, m.p. 110°, $[\alpha]_D^{13}$ +1·5°±1° in $COMe_2$), which is hydrolysed to the *acid* (**IV**), m.p. 211—214°, $[\alpha]_D^{11}$ +3·2°±1° in dioxan. Oxidation (CrO_3 in AcOH) of (**III**) followed by hydrolysis gives the tricarboxylic acid (**V**), m.p. 258—263° (decomp.), $[\alpha]_D^{11}$ +14·9°±1° in dioxan (*anhydride-anilide*, m.p. 188—189°), identical with the product obtained by oxidation of 12-ketocholanic acid with HNO_3 or, preferably, of Me 11-hydroxy-12-ketocholanate with CrO_3 and subsequent hydrolysis. Alternatively (**II**) is transformed by BzO_2H in $CHCl_3$ into *Me* 11(β) : 12(β)-*oxidocholanate*, m.p. 96—97°, $[\alpha]_D^{17}$ +29·4°±2° in $COMe_2$; the corresponding *acid*, m.p. 155—157°, is



(V.)

hydrogenated (Raney Ni under pressure) to a mixture of Me cholanate and (**I**), thus proving the presence of the oxido-ring at $C_{(11)}$–$C_{(12)}$ and showing that it is in the β-position provided that no change of configuration occurs at $C_{(12)}$ during hydrogenating fission. When heated (**IV**) gives a poor yield of the 11-*hydroxy*-12-*lactone*, $C_{24}H_{38}O_3$, m.p. 240—242°, $[\alpha]_D^{17}$ −41·8±2° in C_6H_6, oxidised to the 11-*ketolactone*, $C_{24}H_{36}O_3$, m.p. 152—154°. M.p. are corr. (block). H. W.

Bile acids and related substances. XII. Simplified preparation of pure deoxycholic acid and its derivatives. T. Reichstein and M. Sorkin (*Helv. Chim. Acta*, 1942, **25**, 797—805).—It is proposed to designate deoxycholic acid (**I**) as 3(α) : 12(β)-dihydroxycholanic acid and all other sterol derivatives which have OH at $C_{(12)}$ in the same steric position as 12(β)-OH-derivatives. (**I**), m.p. 176—177°, $[\alpha]_D^{19}$ +47·7°±2° in dioxan, $[\alpha]_D^{17.5}$ +52·8°±2° in EtOH, is best obtained by energetic hydrolysis of the Me ester diacetate, m.p. 118—119°, readily obtained pure from the technical material. The Me ester (**II**), m.p. 80—81°, $[\alpha]_D^{16}$ +55·8°±1° in $COMe_2$, is obtained by the action of 1% HCl–MeOH on (**I**) for 24 hr. at room temp., but is not readily obtained pure from technical (**I**). The 3-acetate (**III**), m.p. 128—128·5°, $[\alpha]_D^{20}$ +65·9°±1° in $COMe_2$, of (**II**) is readily obtained in ~40% yield by partial acetylation (Ac_2O–boiling C_6H_6) of (**II**) from technical (**I**) and the mother-liquors can be worked up for the diacetate (**IV**) by treatment with Ac_2O–C_5H_5N at 100° for 3 hr.; stronger or more protracted heating causes increased darkening. Oxidation of (**III**) by CrO_3 in AcOH gives Me 12-keto-3(α)-acetoxycholanate, m.p. 153·5—154·5°, $[\alpha]_D^{21}$ +104·8°±1·5° in $COMe_2$, in excellent yield, converted by keeping with 1% HCl–MeOH for 1 day almost quantitatively into the 3(α)-OH-ester, m.p. 110—111·5°, $[\alpha]_D^{14.5}$ +96·5°±1·5° in $COMe_2$, and readily hydrolysed by alkali to 3(α)-hydroxy-12-ketocholanic acid, m.p. 160—161°, which is thus obtained more readily than by direct oxidation of (**I**) or through the partly acetylated acid. Partial hydrolysis (1% HCl–MeOH for 1 day) of (**IV**) leads to amorphous Me 3(α)-hydroxy-12(β)-acetoxycholanate, oxidised by CrO_3 to Me 3-keto-12(β)-acetoxycholanate, m.p. 122—123°, $[\alpha]_D^{17}$ +83·0°±1° in $COMe_2$. Only pure (**II**) is suitable for the prep. of Me 3 : 12-diketocholanate, m.p. 131—133°. M.p. are corr. (block). H. W.

Bile acids and related substances. XVI. 3(α) : 12(α)-Dihydroxycholanic (12-*epi*deoxycholic) acid. B. Koechlin and T. Reichstein (*Helv. Chim. Acta*, 1942, **25**, 918—935).—Hydrogenation (PtO_2 in AcOH) of Me 12-keto-3(α)-acetoxycholanate gives almost exclusively Me 12(β)-hydroxy-3(α)-acetoxycholanate, m.p. 124—127°. The 3(α)-hydroxy-12-keto-ester is reduced (H_2, Raney Ni, MeOH) to a difficultly separable mixture of esters which is hydrolysed; fractional crystallisation of the acids then gives a little deoxycholic acid and more 3(α) : 12(α)-*dihydroxycholanic acid* (**I**), m.p. 186—188°, $[\alpha]_D^{17.5}$ +38·4°±2° in dioxan [Me ester (**II**), $[\alpha]_D^{17.5}$ +43·6°±1·5° in $COMe_2$, and its amorphous *diacetate* (**III**), $[\alpha]_D^{17}$ +56·8°±2° in $COMe_2$]. (**II**) is oxidised by CrO_3 in AcOH to Me 3 : 12-diketocholanate, m.p. 133—135°, $[\alpha]_D^{18}$ +90·9°±4° in $COMe_2$. Partial hydrolysis (K_2CO_3–aq. MeOH at room temp.) of (**III**) gives amorphous Me 3(α)-hydroxy-12(α)-acetoxycholanate (and some acid, a colourless resin), oxidised (CrO_3 in AcOH at room temp.) to *Me* 3-*keto*-12(α)-*acetoxycholanate* (**IV**), m.p. 109—111°, $[\alpha]_D^{16}$ +44·1°±2° in $COMe_2$. Comparison of the m.p. and [α] of acids and their derivatives belonging to the 3(α) : 12(α)- and 3(α) : 12(β)-series shows that α-lagodeoxycholic acid (Kishi, A., 1936, 469) is not identical with (**I**) and must have a different constitution, and that 12(α)-OH-compounds of the bile acid series have $[\alpha]_D$ ~10—12° more negative than the corresponding 12(β)-OH-compounds and that with 12(α)-OAc substances the difference is ~38° in the same direction. Attempts are described to amplify the physical observations of Giacomello (A., 1940, II, 130) on the configuration of the bile acids by chemical evidence. (**IV**) is hydrolysed appreciably more rapidly than the 12(β)-compound so that the Ac group in the latter is more hindered but it cannot be decided whether this is due to Me at $C_{(18)}$ or :CH of $C_{(17)}$. It is certain, however, that the length of the side-chain at $C_{(17)}$ has a great influence on the rate of hydrolysis of Ac at $C_{(17)}$ in deoxycholic acid and its derivatives since the similar group in the corresponding ætio acid or in 3(α)-hydroxy-12(β)-acetoxypregnan-20-one is more readily removed. This marked effect is readily explained by assuming that OH at $C_{(12)}$ and Me at $C_{(18)}$ are *trans* but can be brought into line with Giacomello's observations by assuming the long side-chain to be on the same side of the ring system. Bisnordeoxycholic acid is not lactonised when boiled in tetrahydronaphthalene for 2 hr. or distilled at 300°/vac. but the negative evidence is difficult to evaluate. A *Me anhydrobisnordeoxycholate*, m.p. 161—163°, is described. Me 12(α)-hydroxy- and 12-keto-3(α)-acetoxycholanate could not be obtained cryst. M.p. are corr. (block). H. W.

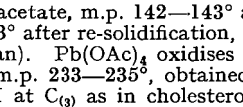
Bile acids and related substances. XIV. 3-Keto-Δ^{11}-cholenic acid and 3-keto-$\Delta^{4:11}$-choladienoic acid. U. Burckhardt and T. Reichstein (*Helv. Chim. Acta*, 1942, **25**, 821—832).—Me diacetyldeoxycholate is converted by partial hydrolysis (K_2CO_3 in aq. MeOH at room temp.) followed by remethylation (CH_2N_2 or 1% HCl–MeOH at room temp.) or, more simply, by direct treatment

with HCl–MeOH into amorphous Me 3(α)-hydroxy-12(β)-acetoxycholanate; this is oxidised to Me 3-keto-12(β)-acetoxycholanate (**I**), m.p. 122—123°, $[\alpha]_D^{21}$ +82·7°±2° in $COMe_2$, hydrolysed to 12(β)-hydroxy-3-ketocholanic acid (**II**), m.p. 100—110° [Me ester (**III**), m.p. 144—145°, $[\alpha]_D^{15}$ +50·5°±1·5° in $COMe_2$]. (**I**) is converted by Br in AcOH into the (?) 4-Br-derivative, m.p. 167—168°, which is transformed by boiling C_5H_5N into *Me* 3-*keto*-12(β)-*acetoxy*-Δ⁴-*cholenate*, m.p. 132—134°, $[\alpha]_D^{17}$ +114·2°±2° in $COMe_2$; the position of the double linking is based on analogy and on the spectroscopically established presence of a αβ-unsaturated keto group. It is hydrolysed to 12(β)-hydroxy-3-keto-Δ⁴-cholenic acid (**IV**), m.p. 230—235° [*Me* ester, (**V**), m.p. 150—152°, $[\alpha]_D^{17}$ +80·9°±4° in $COMe_2$]. Thermal decomp. of (**II**) gives the corresponding *lactone*, m.p. 230°, $[\alpha]_D^{18}$ +20·4°±1·5° in $COMe_2$, and a mixture of acid products from which 3-*keto*-Δ¹¹-*cholenic acid*, m.p. 150—152°, $[\alpha]_D^{12}$ +41·2°±2° in $COMe_2$ [*Me* ester (**VI**), m.p. 125·5—126°, $[\alpha]_D^{14}$ +36·9°±2° in $COMe_2$, and its *semicarbazone*, m.p. 196°], is isolated. (**VI**) is hydrogenated to Me 3-ketocholanate, m.p. 116—117°, but unexpectedly reacts with 2 mols. of BzO_2H with formation of an (?) *oxidolactonic* ester, $C_{25}H_{38}O_5$, m.p. 122—123°, $[\alpha]_D^{17\cdot5}$ +38·1°±4° in $COMe_2$. Thermal decomp. of (**IV**) yields a small amount of the corresponding lactone and a mixture of acids from which 3-keto-Δ⁴:¹¹-choladienoic acid, m.p. 202—204°, is isolated directly or through its *Me* ester (**VII**), m.p. 114—115°, $[\alpha]_D^{17}$ +99·7°±4° in $COMe_2$. (**VII**) and BzO_2H in $CHCl_3$ in the dark and at room temp. give *Me* 3-*keto*-11 : 12-*oxido*-Δ⁴-*cholenate*, m.p. 152—155°, $[\alpha]_D^{16}$ +91·7°±4° in $COMe_2$. Bromination of (**III**) and treatment of the product with boiling C_5H_5N gives (**V**). M.p. are corr. (block). H. W.

Steroid α-ketols. III. Partial synthesis of 3 : 17-diacetoxy-Δ⁵-androsten-16-one. F. H. Stodola and E. C. Kendall (*J. Org. Chem.*, 1942, **7**, 336—340).—The condensation product of dehydroandrosterone and COMeEt (Butenandt *et al.*, A., 1939, II, 165) is reduced by $Pr^{\beta}OH$–$Al(OPr^{\beta})_3$ in boiling C_6H_6 and then acetylated (Ac_2O in C_5H_5N at 40°) to 3 : 17-*diacetoxy*-16-iso*butylidene*-Δ⁵-*androstene*, m.p. 138—139°. This is converted by OsO_4 into the corresponding *glycol*, two forms, m.p. 195—205° and 150—152°, and the latter is oxidised by $Pb(OAc)_4$ in dry C_6H_6 to 3 : 17-*diacetoxy*-Δ⁵-*androsten*-16-*one* (**I**), m.p. 124—125°, identical with the substance described by Butenandt (*loc. cit.*). Dehydro*iso*androsterone acetate, PhCHO, and NaOMe in boiling MeOH afford 16-*benzylidene*iso*androsterone*, m.p. 202—205°, which is reduced [$Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$], treated with KOH, and then acetylated to 3 : 17-*diacetoxy*-16-*benzylidene*-Δ⁵-*androstene*, m.p. 127—129°. This is converted by OsO_4 into the *glycol*, m.p. 204—206°, cleaved by $Pb(OAc)_4$ in C_6H_6 to (**I**). Androstene-3 : 17-dione 3-enol Et ether is transformed by $Bu^{\alpha}O{\cdot}NO$ in C_6H_6–EtOH containing NaOEt followed by aq. H_2SO_4 into 16-*oximino*-Δ⁴-*androstene*-3 : 17-*dione*, softens at 230°, m.p. 237—238° (decomp.), reduced (Zn dust and AcOH at 50°) and then acetylated to 16-ketotestosterone acetate, m.p. 194—195° (cf. A., 1942, II, 103). H. W.

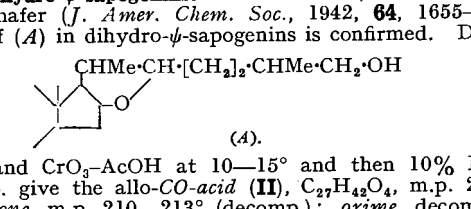
Constituents of the adrenal cortex and related substances. LVI. "Substance *V*" and determinations of configuration in the $C_{21}O_5$ group. J. von Euw and T. Reichstein (*Helv. Chim. Acta*, 1942, **25**, 988—1022).—On the basis of chemical and optical evidence configurations are ascribed to all the 8 substances of the $C_{21}O_5$ group hitherto isolated from the adrenal cortex. Substance *A* is chosen as reference compound since it is the most highly hydrogenated member and has the most centres of symmetry; the centre at $C_{(20)}$ remains undefined. Substances *A*, *C*, *V*, *D*, *E*, *U*, *M*, and *Fa* are respectively *allo*pregnane-3(β) : 11(β) : 17(β) : 20 (?) : 21-pentaol, -3(α) : 11 (?) : 17(β) : 21-tetraol-20-one, -3(β) : 11(β) : 17(β) : 21-tetraol-20-one, -3(β) : 17(β) : 21-triol-11 : 20-dione, Δ⁴-pregnene-11(β) : 17(β) : 20 (?) : 21-tetraol-3-one, -17(β) : 20 (?) : 21-triol-3 : 11-dione, -11(β) : 17(β) : 21-triol-3 : 20-dione, and -17(β) : 21-diol-3 : 11 : 20-trione. The undefined asymmetry centre at $C_{(20)}$ is the same in *A*, *E*, and *U*. The sterical position of OH at $C_{(11)}$ in *C* is uncertain. Fractional crystallisation of samples $C_{17}BI$ and $C_{17}BII$ (A., 1936, 1382) leads to the isolation of pure *C*, new m.p. 273—276° (decomp.), $[\alpha]_D^{15}$ +73·1°±4°, $[\alpha]_{5461}^{15}$ +90·2°±4° in abs. EtOH, $[\alpha]_D^{18}$ +59·2°±5°, $[\alpha]_{5461}^{18}$ +75·7°±5° in dioxan [*C* diacetate (**I**), m.p. 204—205°, $[\alpha]_D^{15}$ +73·8°±2°; $[\alpha]_{5461}^{15}$ +90·5°±2° in dioxan], and *D*, new m.p. 238—242° (decomp.), $[\alpha]_D^{16}$ +61·8°±2°, $[\alpha]_{5461}^{16}$ +78·7°±2° in dioxan; the residues from these substances are acetylated and purified chromatographically, thereby giving *inter alia* (**I**), *D* diacetate (**II**), m.p. 223—224°, $[\alpha]_D^{15}$ +72·3°±2°, $[\alpha]_{5461}^{15}$ +84·7°±2° in dioxan, and *V diacetate* (**III**), m.p. 225—227°, $[\alpha]_D^{18}$ +62·6°±2°, $[\alpha]_{5461}^{17}$ +77·3°±2° in dioxan, which immediately reduces Ag_2O–NH_3 at room temp. (**III**) is hydrolysed (K_2CO_3 in aq. MeOH at room temp.) to *substance V*, m.p. 220—225°, $[\alpha]_D^{13}$ +50·7°±3°, $[\alpha]_{5461}^{13}$ +68·0°±3° in dioxan, which like *A*, *C*, and *D* is oxidised by excess of CrO_3 at room temp. to androstane-3 : 11 : 17-trione. (**II**) is essentially unchanged when treated with CrO_3 (1 mol.) in AcOH at room temp. whereas (**III**) is smoothly transformed into (**II**) showing that *V* and *D* differ in the function of the O atom at $C_{(11)}$. (**I**) gives allo*pregnane*-3(α) : 17(β) : 21-*triol*-11 : 20-*dione* 3 : 21-*diacetate*, m.p. 222—224°, $[\alpha]_D^{12}$ +93·6°±3°, $[\alpha]_{5461}^{12}$ +113·8°±3° in dioxan. *V* is degraded by HIO_4 to 3(β) : 11(β) : 17(β)-trihydroxyætio*allo*cholanic acid (**IV**), characterised as the Me ester, m.p. 253—254°, $[\alpha]_D^{13}$ +7·6°±3°, $[\alpha]_{5461}^{13}$ +8·3°±3° in dioxan (3-acetate, m.p. 142—143° after becoming opaque at 100° and 152—153° after re-solidification, $[\alpha]_D^{14}$ +11·4°±3°, $[\alpha]_{5461}^{14}$ +5·1°±2° in dioxan). $Pb(OAc)_4$ oxidises (**IV**) to androstane-3(β) : 11(β-)diol-17-one, m.p. 233—235°, obtained previously from *A* and containing β-OH at $C_{(3)}$ as in cholesterol. *D* is similarly oxidised to 3(β) : 17(β)-dihydroxy-11-ketoætio*allo*cholanic acid (Kendall's acid 5*B*), m.p. 298—301° (decomp.) [Me ester (**V**), m.p. 235—237°, $[\alpha]_D^{15}$ +23·4°±2°, $[\alpha]_{5461}^{15}$ +29·3°±2° in dioxan, and its acetate, m.p. 156—157°, $[\alpha]_D^{14}$ +14·8°±2°, $[\alpha]_{5461}^{14}$ +14·8°±2° in dioxan]. (**V**) is oxidised (CrO_3 in AcOH at room temp.) to *Me* 17(β)-*hydroxy*-3 : 11-*diketoæt*io*allocholanate* (**VI**), m.p. 216—217°, $[\alpha]_D^{13}$ +50·0°±2°, $[\alpha]_{5461}^{13}$ +61·0°±2° in dioxan, also obtained from (**IV**) (Me ester) and AcOH–CrO_3. *C* is oxidised (HIO_4) and then methylated to Me 3(α) : 11(? β) : 17(β)-trihydroxyætio*allo*cholanate (**VII**), m.p. 229—231°, $[\alpha]_D^{14}$ +15·0°±3°, $[\alpha]_{5461}^{14}$ +18·0°±3° in dioxan [3-acetate (**VIII**), m.p. 186—187·5°, $[\alpha]_D^{15}$ +19·5°±2°, $[\alpha]_{5461}^{15}$ +23·9°±2° in dioxan]. (**VIII**) is oxidised (CrO_3) to *Me* 3(α) : 17(β)-*dihydroxy*-11-*ketoæt*io*allocholanate* 3-*monoacetate*, m.p. 208—209°, $[\alpha]_D^{14}$ +38·0°±2°, $[\alpha]_{5461}^{14}$ +47·0°±2° in $COMe_2$, whereas (**VII**) affords (**VI**). Attempted hydrogenation (PtO_2 in AcOH) of (**III**) gives ill-defined results. Pure *C* is not pptd. by digitonin, which reacts distinctly with *V* and particularly with *D*. *A* is oxidised by HIO_4 to (presumably) an aldehyde (**IX**), further transformed by the successive action of aq. $Bu^{\gamma}OH$–Br and CH_2N_2 into (**VI**). Oxidation (Ag_2O) of (**IX**) leads to an unidentified acid characterised as the *Me* ester *acetate*, $C_{24}H_{34}O_6$, m.p. 215—217° becoming complete at 223°, and an unidentified neutral *product*, m.p. 230—232°. *M* and HIO_4 afford 11(β) : 17(β)-dihydroxy-3-keto-Δ⁴-æ-tiocholenic acid, m.p. 235—245° (decomp.) (Me ester, m.p. 207—208°, $[\alpha]_D^{14}$ +111·5°±2°, $[\alpha]_{5461}^{14}$ +135·2°±2° in dioxan), hydrogenated to the Me ester of (**IV**). The following data are recorded : *allo*pregnane-3(β) : 17(β) : 21-triol-20-one 3 : 21-diacetate (*P* diacetate), m.p. 208—209°, $[\alpha]_D^{18}$ +44·5°±3°, $[\alpha]_{5461}^{18}$ +57·4°±3° in dioxan; *allo*pregnane-3(β) : 17(α) : 21-triol-20-one 3 : 21-diacetate (17-*isoP* diacetate), m.p. 159—161°, $[\alpha]_D^{19}$ −68·1°±4°, $[\alpha]_{5461}^{19}$ −89·7°±4° in dioxan; androstane-3(β) : 11(β)-diol-17-one, m.p. 234—235°, $[\alpha]_D^{19}$ +81·3°±2°, $[\alpha]_{5461}^{19}$ +104·9°±2° in dioxan (3-acetate, m.p. 228—229°, $[\alpha]_D^{19}$ +70·5°±2°, $[\alpha]_{5461}^{19}$ +87·1°±2° in dioxan); androstan-3(β)-ol-17-one, m.p. 176—177°, $[\alpha]_D^{15}$ +81·1°±1°, $[\alpha]_{5461}^{15}$ +100·6°±1° in dioxan (acetate, m.p. 104—105°, $[\alpha]_D^{15}$ +64·6°±1°, $[\alpha]_{5461}^{15}$ +80·0°±1° in dioxan); androstan-3(α)-ol-17-one (androsterone), m.p. 185—185·5°, $[\alpha]_D^{15}$ +87·8°±1·5°, $[\alpha]_{5461}^{15}$ +107·3°±1·5° in dioxan (acetate, m.p. 164·5—165·5°, $[\alpha]_D^{14}$ +76·7°±1°, $[\alpha]_{5461}^{14}$ +92·4°±1° in dioxan); *allo*pregnane-3(β) : 11 : 21-triol-20-one 3 : 21-diacetate (*R* diacetate), m.p. 173—174°, $[\alpha]_D^{17}$ +83·7°±2°, $[\alpha]_{5461}^{17}$ +102·7°±2° in dioxan, $[\alpha]_D^{18}$ +92·4°±2°, $[\alpha]_{5461}^{18}$ +114·3°±2° in $COMe_2$; *allo*pregnane-3(β) : 21-diol-20-one diacetate, m.p. 153—154°, $[\alpha]_D^{17}$ +77·1°±2°, $[\alpha]_{5461}^{17}$ +93°±2° in $COMe_2$, $[\alpha]_D^{19}$ +77·9°±2°, $[\alpha]_{5461}^{19}$ +94·4°±2° in dioxan; progesterone, m.p. 129—130°, $[\alpha]_D^{19}$ +174·6°±2°, $[\alpha]_{5461}^{19}$ +214·7°±2° in $COMe_2$; corticosterone acetate, m.p. 145—146°, $[\alpha]_D^{18}$ +200°±2°, $[\alpha]_{5461}^{18}$ +245°±2° in dioxan; deoxycorticosterone acetate, m.p. 158—160°, $[\alpha]_D^{19}$ +173·6°±2°, $[\alpha]_{5461}^{19}$ +211·9°±2° in dioxan, $[\alpha]_D^{18}$ +164·3°±2°, $[\alpha]_{5461}^{18}$ +199·8°±2° in $COMe_2$; androstane-3 : 17-dione, m.p. 131—132°, $[\alpha]_D^{20}$ +107·1°±2°, $[\alpha]_{5461}^{20}$ +132·5°±2° in $COMe_2$, $[\alpha]_D^{18}$ +113·5°±2°, $[\alpha]_{5461}^{18}$ +138·0°±2° in $CHCl_3$; androstan-3(β)-ol-11 : 17-dione acetate, m.p. 162—163°, $[\alpha]_D^{29}$ +96·2°±2°, $[\alpha]_{5461}^{20}$ +117·6°±2° in dioxan; *allo*pregnane-3(β) : 21-diol-11 : 20-dione diacetate (*N* diacetate), m.p. 144—145°, $[\alpha]_D^{19}$ +85·6°±2°, $[\alpha]_{5461}^{19}$ +105·6°±2° in dioxan; dehydrocorticosterone acetate, m.p. 179—181°, $[\alpha]_D^{18}$ +233·7°±2°, $[\alpha]_{5461}^{18}$ +285·1°±2° in dioxan. M.p. are corr. (block). H. W.

Sterols. CXLVIII. Sapogenins. LXII. Structure of the side-chain in dihydro-ψ-sapogenins. R. E. Marker, D. L. Turner, and P. R. Ulshafer (*J. Amer. Chem. Soc.*, 1942, **64**, 1655—1658).—Presence of (*A*) in dihydro-ψ-sapogenins is confirmed. Dihydro-ψ-



(*A*).

tigogenin and CrO_3–AcOH at 10—15° and then 10% NaOH at room temp. give the allo-*CO-acid* (**II**), $C_{27}H_{42}O_4$, m.p. 207—209° [*semicarbazone*, m.p. 210—213° (decomp.); *oxime*, decomp. 232—234°; *Me* ester, m.p. 138°], and Δ¹⁶-*allo*pregnene-3 : 20-dione [obtained also by further oxidation of (**II**) at 28—30°]. Dihydro-ψ-sarsasapogenin gives (cf. A., 1940, II, 171) similarly the isomeric



(II.)

CO-acid (**III**) [as (**II**) but $C_{(5)}$ inverted], m.p. 233—236° [*semicarbazone*, decomp. 236°; *oxime*, m.p. 232—234°; *Me* ester (**IV**), *forms*, m.p. 116·5° and 85—87° (*semicarbazone*, decomp. 225)], and Δ¹⁶-

pregnene-3 : 20-dione. Na–EtOH reduces (**IV**) to *epi*dihydro-ψ-sarsasapogenin. Zn–Hg–conc. HCl–EtOH reduces (**III**) to the *acid*, $C_{27}H_{44}O_3$ [as (**III**), CH_2 replacing CO], m.p. 81·5—82·5°. H_2–PtO_2 reduces (**III**) to the 3(α)-, m.p. 181—183° (*acetate*, m.p. 197—199°), and some 3(β)-*OH-acid*, $C_{27}H_{44}O_4$, m.p. 189—190° (digitonide), but (**II**) gives only the 3(β)-*OH*-allo-*acid*, m.p. 240—241° (*acetate*, m.p. 179—181°). R. S. C.

Lactones related to the cardiac aglycones. VIII. β-Substituted $\Delta^{\alpha\beta}$-butenolides of the naphthalene and indene series.—See A., 1942, II, 405.

Lactones related to the cardiac aglycones. VII. Synthesis of 3 : 14-bisdeoxythevetigenin and of 14-deoxythevetigenin. J. Fried, R. G. Linville, and R. C. Elderfield (*J. Org. Chem.*, 1942, **7**, 362—373).—Dehydrocholic acid is reduced by Zn–Hg and conc. HCl in AcOH to cholanic acid, m.p. 163—164°, which is degraded according to Wieland *et al.* (A., 1926, 1139) to ætiocholanic acid. The corresponding chloride, m.p. 80—86°, is transformed by CH_2N_2 into 21-diazopregnan-20-one, m.p. 80—106°, which does not give a cryst. product when warmed with AcOH. With HCl it readily yields 21-*chloropregnan-20-one*, m.p. 103—105° (corr.), $[\alpha]_D^{25}$ +125° ±2° in $CHCl_3$, which does not give a cryst. substance with NaOAc or KOAc but with NaOBz in boiling aq. EtOH affords 21-*benzoyloxypregnan-20-one* (**I**), m.p. 158—159° (corr.), $[\alpha]_D^{25}$ 113°±2° in $CHCl_3$. (**I**) is converted by $CH_2Br{\cdot}CO_2Et$ and Zn in boiling C_6H_6 followed by AcOH–HBr at 135—145° into 3 : 14-*bisdeoxythevetigenin* [21-*hydroxy*-$\Delta^{20:22}$-*norcholenolactone* or 3 : 14-*bisdeoxydigitoxigenin*] (**II**), m.p. 167—168°, $[\alpha]_D^{25}$ +11°±1·5° in MeOH. (**II**) gives a strong, positive Legal colour test, indistinguishable from that displayed by the natural cardiac aglycones. The similarity of its ultra-violet absorption curve with those of strophanthidin and periplogenin is strong confirmation for assigning the side-chain double linking of the natural aglycones to the $\Delta^{\alpha\beta}$-position. Catalytic hydrogenation (PtO_2 in EtOH) of (**II**) leads to hexahydrodianhydrothevetigenin, m.p. 187—189° (corr.), $[\alpha]_D$ +33·0°, identical with that derived from digitoxigenin, sarmentogenin, or digoxigenin. Pregnanedione is selectively hydrogenated (Pt, 90% AcOH) at $C_{(3)}$ to a mixture of isomeric pregnanolones from which pregnan-3(β)-ol-20-one is isolated in 30—35% yield by pptn. with digitonin. The 21-CHPh: derivative acetate, m.p. 172—174° (corr.), is transformed by CrO_3 in AcOH at 50° and then at 60—70° into 3(β)-acetoxyætiocholanic acid, m.p. 177—179° (corr.). This is converted into 21-diazo-3(β)-acetoxypregnan-20-one (**III**), a liquid, which with HCl in dry Et_2O affords 21-*chloro*-3(β)-*acetoxypregnan-20-one*, m.p. 115—116° (corr.) [the 21-*Br*-compound has m.p. 139—141° (corr.), $[\alpha]_D^{25}$ +100°±5° in $CHCl_3$]. (**III**) and AcOH at 100° yield pregnane-3(β) : 21-diol-20-one diacetate, m.p. 111—112° (corr.) (lit. 145—146°), $[\alpha]_D^{27}$ +91°±4° in $CHCl_3$, which with $CH_2Br{\cdot}CO_2Et$ and Zn affords 14-*deoxythevetigenin acetate* (**IV**), m.p. 197—198°, $[\alpha]_D^{26}$ +11·3° ±1° in $CHCl_3$, and 20 : 21-*dihydroxy*-3(β)-*acetoxynorcholanolactone*, m.p. 196—200° (corr.), converted into (**IV**) by boiling AcOH. 14-*Deoxythevetigenin* has m.p. 220—222°, $[\alpha]_D$ +11·5°±1·5° in $CHCl_3$. H. W.

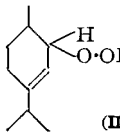
Lactones related to the cardiac aglycones. IX. β-Substituted-$\Delta^{\alpha\beta}$-butenolides of the norcholane series. W. S. Knowles, J. Fried, and R. C. Elderfield (*J. Org. Chem.*, 1942, **7**, 383—388).—Cholanyl chloride is converted into the amorphous CHN_2 ketone and thence into *norcholanyl* CH_2Cl *ketone*, m.p. 109—110°, $[\alpha]_D^{27}$ +24° in $CHCl_3$, which with KOAc in boiling AcOH affords *norcholanyl* $OAc{\cdot}CH_2$ *ketone*, m.p. 81·5—82·5°, $[\alpha]_D^{27}$ +22° in $CHCl_3$. This with Zn and $CH_2Br{\cdot}CO_2Et$ and subsequently with HBr–AcOH at 135—140° yields β-*norcholanyl*-$\Delta^{\alpha\beta}$-*butenolide* (**I**), m.p. 162—163°, $[\alpha]_D^{25}$ +21° in $CHCl_3$. The change is better effected with boiling Ac_2O, which is shown to convert β-hydroxy-β-*cyclo*hexylbutyrolactone into its *acetate*, m.p. 93—95°, which passes at 200° into β-*cyclo*hexyl-$\Delta^{\alpha\beta}$-butenolide. Me triacetylcholate is partly hydrolysed by 0·451N-KOH–EtOH to 7 : 12-*diacetylcholic acid* (**II**), m.p. 204—204·5°, $[\alpha]_D^{28}$ +71° in MeOH, which is further acetylated (Ac_2O–C_5H_5N at room temp. and finally at 100°) to triacetylcholic acid [cryst. products are not obtained from (**II**) and AcCl–AcOH or from cholic acid and keten]; this does not give a cryst. chloride and the corresponding CHN_2, CH_2Cl (**III**), and $CH_2{\cdot}OAc$ ketones are also non-cryst. (**III**) and NaOBz afford *triacetylnorcholyl* $OBz{\cdot}CH_2$ *ketone*, m.p. 178—180·5° $[\alpha]_D^{27}$ +63° in $CHCl_3$, from which a butenolide could not be obtained by the action of $CH_2Br{\cdot}CO_2Et$ and Zn although the crude product gives a strong Legal test. Only amorphous compounds result from the action of CH_2N_2 (1 mol.) on triformylcholyl chloride and treatment of the product with HCl. With excess of CH_2N_2 the product appears to be *norcholyl* CH_2Cl *ketone*, m.p. 191·5—192·5°, $[\alpha]_D^{17}$ +39° in MeOH. M.p. are corr. (**I**) shows no activity in frogs. H. W.

V.—TERPENES AND TRITERPENOID SAPOGENINS.

Absorption spectra of terpenoid compounds. III. Thiosemicarbazones of irone, eucarvone, and related ketones. IV. Five-atom-ring unsaturated ketones. A. E. Gillam and T. F. West (*J.C.S.*, 1942, 483—486, 486—488; cf. A., 1942, I, 163).—III. By means of the thiosemicarbazones it is shown that English and French irone each contain two ketones of differing composition (cf. A., 1941, II, 327 and *loc. cit.*, and Ruzicka, A., 1942, II, 99). The thiosemicarbazones, m.p. 180° to 184—185° and indefinite (110—130°), have similar absorption max., but extinction coeffs. are the same only if mol. wts. are assumed to be 279 and 293, respectively. The max. at 3010 A. conforms to Woodward's rule (A., 1941, II, 197) for substances containing CH:CH·CH:N. Heating irone in 20% H_2SO_4 changes the absorption max. to ~3100 A., as expected for formation of C:C·C:C·CO, but the change later progresses spontaneously, indicating formation by the acid of > one substance, of which some at least are labile. Eucarvone and its *thiosemicarbazone*, m.p. 163—164°, have absorption max. at 3035 (ε 6300) and 3310 A. (ε 22,750), respectively, in conformity with Woodward's rule (CH:CH·CH·CR·CO); dihydroeucarvone similarly has absorption max. at 2395 (ε 7250) and 3080 A. (ε 137) (C:CR·CO) and its semicarbazone has a max. at 2645 A. (ε 18,500).

IV. The following absorption max. show that five-membered ring ketones do not obey Woodward's rules. *iso*Thujone thus probably has the accepted structure (cf. A., 1942, II, 106). Dihydrojasmone 2370 (ε 12,200) and 3040 A. (ε 55) and its semicarbazone 2665 A. (ε 20,400); tetrahydropyrethrolone 2320 A. (ε 11,540—12,700) and its semicarbazone 2650 A. (ε 21,770—22,500). R. S. C.

Autoxidation of hydrocarbons. IV. *p*-Menthene peroxide and methylated peroxides. H. Hock and S. Lang (*Ber.*, 1942, **75**, [*B*], 300—313).—*dl*-Menthol is converted by anhyd. $ZnCl_2$ into *dl*-Δ³-*p*-menthene (**I**), b.p. 55°/14 mm., with a small proportion of dimenthene, $(C_{10}H_{18})_2$, b.p. 109—110°/0·2 mm. Autoxidation of (**I**), best at 50° and under the influence of ultra-violet light, gives ~15% of 2-*dl*-Δ³-p-*menthenyl H peroxide* (**II**), b.p. 57·5°/0·05 mm., with smaller quantities of dl-*menthene* 3 : 4-*oxide* (**III**), b.p. 45—47°/1·0 mm., and dl-Δ³-*menthen*-2-*ol* (**IV**).



(II.)

(**II**) is smoothly reduced by Na_2SO_3 to carvenol [=(**IV**)], b.p. 64°/0·4 mm., oxidised by CrO_3 to *dl*-carvenone (semicarbazone, m.p. 200—201°). (**III**) is converted by dil. acid at 110—120° (sealed tube) into trans-*menthane*-3 : 4-*diol*, b.p. 85°/0·4 mm., m.p. 95°. 1-Methyl-1 : 2 : 3 : 4-tetrahydro-1-naphthol, m.p. 88°, and anhyd. $ZnCl_2$ at 100° give a mixture of 1-methyl-3 : 4-dihydro-, 1-methylene-1 : 2 : 3 : 4-tetrahydro-, and 1-methylnaphthalene; this is reduced by Na and $C_5H_{11}{\cdot}OH$ at 140—150° to 1-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 87—88°/7 mm. Tetrahydronaphthyl H peroxide could not be methylated by CH_2N_2 but is converted by Me_2SO_4 and alkali at definite p_H into *tetrahydronaphthyl Me peroxide* (**V**), b.p. 72·5°/0·3 mm., violent decomp. 140°, which gives notable amounts of CH_2O when heated; in consequence of the stabilising action of Me it exhibits only feeble peroxide character. Δ²-cyclo*Hexenyl Me peroxide*, b.p. 19·5°/1 mm., decomposes at ~130° with liberation of CH_2O in only small amount so that action is not similar to that of (**V**). p-*Menthenyl Me peroxide*, b.p. 33—34°/0·01 mm., decomposes at ~140° giving CH_2O and menthenol, which is partly dehydrated to menthadiene. The methylated peroxides are moderately stable to alkali hydroxide and far more stable than the initial autoxidised material. H. W.

Tertiary bases and betaines from piperitone oxide.—See A., 1942, II, 408.

Presence of piperitenone and *iso*piperitenone in the oil of Moroccan pennyroyal.—See A., 1942, III, 862.

Volatile plant substances. XVII. Synthesis of *dl*-Δ⁴-carene from piperitenone. Y. R. Naves and G. Papazian (*Helv. Chim. Acta*, 1942, **25**, 984—988).—The identity of the hydrocarbon obtained by reduction (Wolff–Kishner) of piperitenonehydrazone (Naves, A., 1942, III, 862) as *dl*-Δ⁴-carene is confirmed by identification of *dl-cis*-3 : 3-dimethyl-2-γ-hydroxybutyl*cyclo*propanecarboxylic and *dl*-caronic acid as products of its oxidation. H. W.

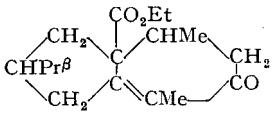
Volatile plant substances. XVIII. Absorption of piperitenone and related ketones in the ultra-violet. Y. R. Naves and G. Papazian (*Helv. Chim. Acta*, 1942, **25**, 1023—1035).—The prep. of piperitenone [$\Delta^{1:4(8)}$-*p*-menthadien-3-one] (**I**) from its mixture (**II**) with *iso*piperitenone through the compound with $NaHSO_4$ and by means of NaOEt in EtOH is described. Ozonolysis of (**I**) in AcOH–EtOAc gives only negligible amounts of CH_2O. (**II**) is transformed by HCO_2H into 3-methyl-Δ²-*cyclo*hexenone (**III**), b.p. 52—52·5°/1·6 mm. (semicarbazone, m.p. 198·5—199°). *l*-Piperitone from *Eucalyptus dives* is racemised by NaOEt–EtOH and converted into the α-, m.p. 225—226°, and β-, m.p. 174—176°, -semicarbazones, from the former of which *dl*-piperitone (**IV**), b.p. 80°/1·8 mm., is obtained. (**I**) does not appear to react with Girard's reagent *P*. The colour reactions of (**I**), (**IV**), and pulegone (**V**) are tabulated. The ultra-violet absorption spectra of (**I**) in EtOH and hexane have been studied in parallel with those of (**III**), (**IV**), and (**V**) and compared with those of mesityl oxide, phorone, and other αα′-diethylenic ketones. M.p. are corr. H. W.

Dibromo*epi*camphor. J. M. Montañés del Olmo (*Anal. Fis. Quím.*, 1941, **37**, 604—608).—Oxidation (CrO_3–AcOH or $K_2Cr_2O_7$–

H_2SO_4) of dibromopinene yields probably *dibromoepicamphor* (2 : 4-*dinitrophenylhydrazone*, m.p. 182°). F. R. G.

Dependence of optical rotatory power on chemical constitution. XX. Stereoisomeric xylidinomethylenecamphors. B. K. Singh and B. Bhaduri (*Proc. Indian Acad. Sci.*, 1942, **16, A**, 62—67; cf. A., 1940, II, 377).—The hydroxymethylenecamphor and base in AcOH–MeOH afford d-, $[\alpha]_D$ +332·7° in MeOH, l-, $[\alpha]_D$ −332·5° in MeOH, and dl-m-5′-, all m.p. 165—167°, and d-, m.p. 123—124°, $[\alpha]_D$ +317·7° in MeOH, l-, m.p. 123—124°, $[\alpha]_D$ −318° in MeOH, and dl-p-, m.p. 101°, *-xylidinomethylenecamphor*. The rotatory powers of the respective *d*- and *l*-forms are identical and follow the simple Drude dispersion law. Substitution of H by Me in the Ph group of anilinomethylenecamphor lowers its rotatory power, and introduction of a second Me lowers it further. A. T. P.

Azulenes. I. Synthesis of vetivazulene. R. R. Coats and J. W. Cook (*J.C.S.*, 1942, 559—562).—Hydrogenation (Raney Ni at 180°/100 atm.) of *p*-$C_6H_4Pr^{\beta}$·OH gives 4-*iso*propyl*cyclo*hexanol, b.p. 102—110°/15 mm., oxidised by 50% aq. $HNO_3 + NH_4NO_3$ at 50—55° to β-*iso*propyladipic acid, the Et ester of which with Na–PhMe affords Et 4-*iso*propyl*cyclo*pentanone-2-carboxylate (**I**), b.p. 128—135°/15 mm., and thence (boiling 3N-HCl) 3-*iso*propyl*cyclo*pentanone (**II**), b.p. 75—80°/15 mm. When Δ^{β}-hexen-δ-one (**III**) is added to (**II**) and $NaNH_2$–Et_2O (in N_2) at room temp., then under reflux, (probably) 5-3′-*iso*propyl*cyclo*pentylidene-3-*iso*propyl*cyclo*pentanone (**IV**) is formed, also obtained from (**II**) and $NaNH_2$–Et_2O at −20°. Hydrogenation (Pd-black–$COMe_2$) of (**IV**) affords the saturated ketone (*semicarbazone*, m.p. 161·5°; oxime, m.p. 142—143·5°). (**III**) condenses readily with the Na derivative of (**I**) in EtOH at room temp., giving a mixture of esters (**V**), b.p. 179—190°/12 mm., saponified and decarboxylated by boiling KOH–EtOH to unsaturated ketones, b.p. 160—170°/14 mm., hydrogenated (Pd-black–EtOH) to a mixture of stereoisomeric ketones; the latter afforded a *semicarbazone* (**VI**), m.p. 204—205°, and an *oxime*, m.p. 154·5°, and (**VI**) gave 4 : 7-*dimethyl*-2-iso*propyl*-5-*hydrindanone* (**VII**), distils at 0·3 mm. (bath at 100°). (**VII**) is probably identical with the product obtained by degradation of tetrahydro-β-vetivone (cf. Pfau *et al.*, A., 1941, II, 137), and is dehydrogenated (Pd-black at 290—300° in an evacuated sealed tube) to 4 : 7-dimethyl-2-*iso*propyl-5-indanol (**VIII**), new m.p. 133—134° (3 : 5-*dinitrobenzoate*, m.p. 145—146°). (**VII**) and CrO_3–AcOH at 75° gave an acidic product, the *semicarbazone* (**IX**), m.p. 181—182°, of which is converted by aq. H_2SO_4–EtOH, followed by saponification of the ester, into β-(2-*acetyl*-4-iso*propyl*cyclo*pentyl*)*butyric acid*, m.p. 64—65° (p-*phenylphenacyl* ester, m.p. 75—76°). Similar oxidation etc. of the stereoisomeric ketones obtained after separation of (**VI**) gives (**IX**), and the *semicarbazone*, m.p. 151—155°, of a stereoisomeric keto-acid (a gum) (p-*phenylphenacyl* ester, m.p. 66—67°); a neutral fraction (**X**), b.p. 145—155°/12 mm., is recovered from the oxidation. (**VII**) and CH_2N_2 afford an isomeric ketone [*semicarbazone*, m.p. 167—168°, also obtained from (**X**)–CH_2N_2]; although tetrahydro-β-vetivone is not isolated, the crude ketone from (**X**) and Se at 280—310° yield (**VIII**) and vetivazulene, isolated as the *s*-$C_6H_3(NO_2)_3$ complex, m.p. 150—151·5° (cf. *loc. cit.*). A. T. P.

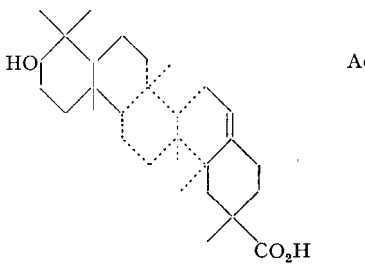

(V.)

Sesquiterpenes. LIV. Preparation of 4 : 8-dimethylazulene-6-carboxylic acid. P. A. Plattner and H. Roniger (*Helv. Chim. Acta*, 1942, **25**, 1077—1085).—Repeated treatment of 4 : 7-dimethylindane with CHN_2·CO_2Et at 140—165° gives a product from which 4 : 8-dimethylazulene (**I**) [additive compound, m.p. 179—180°, with *s*-$C_6H_3(NO_2)_3$] is removed by fractional distillation. The residual ester is worked up for *Et* 4 : 8-*dimethylazulene*-6-*carboxylate*, m.p. 60·5° (*picrate*, m.p. 82—83°), either by chromatography (Al_2O_3–*cyclo*hexane) of its additive *compound*, m.p. 92°, with *s*-$C_6H_3(NO_2)_3$ or by extraction with 85% H_3PO_4. 4 : 8-*Dimethylazulene*-6-*carboxylic acid* (**II**), m.p. 265° after incipient decomp. at 230° [additive *compound* with *s*-$C_6H_3(NO_2)_3$, incipient decomp. ~185°, m.p. ~215°], gives (CH_2N_2) a *Me* ester, m.p. 66·5° [*picrate*, m.p. 103°; additive *compound*, m.p. 127—128°, with *s*-$C_6H_3(NO_2)_3$]. Decarboxylation of (**II**) to (**I**) does not occur smoothly when (**II**) is heated at atm. pressure alone or in presence of $Ca(OH)_2$ but takes place readily in presence of Cu powder. H. W.

Diterpenes. LIV. Synthesis of 8-azaretene. L. Ruzicka and L. Sternbach [with C. Kauter] (*Helv. Chim. Acta*, 1942, **25**, 1036—1037; cf. A., 1941, II, 262).—1 : 6-$C_{10}H_6Me$·NH_2 is condensed with $Pr^{\beta}CHO$ and $AcCO_2H$ in boiling MeOH to a mixture of 8-azaretene-5-carboxylic acid and its H_4-derivative. The mixture is freed from resinous by-products through the NH_4 salts and then dehydrogenated and decarboxylated by Pd–C at 340° to 8-azaretene, m.p. 117·5—118·5° [picrate, m.p. 190—196° (decomp.) according to mode of heating], identical with the compound obtained (*loc. cit.*) from abietic acid. H. W.

Recent progress in terpene chemistry. W. Hückel (*Angew. Chem.*, 1942, **55**, 227—232).—A lecture.

Sapogenins. XIII. Position of the double bond in acids of the β-amyrin group. XIV. Constitution of glycyrrhetic acid and its relation to oleanolic acid. XV. Siaresinolic acid. P. Bilham, G. A. R. Kon, and W. C. J. Ross. **XVI. Acids of elemi resin.** P. Bilham and G. A. R. Kon (*J.C.S.*, 1942, 532—534, 535—539, 540—544, 544—550).—XIII. A new structural formula is put forward to explain the chemistry of the β-amyrin group of triterpenes; the parts of the mol. which have been completely elucidated in previous work are shown in full lines. Reactions of compounds are discussed on the basis of the formula.


(II.)

XIV. Glycyrrhizinum ammoniacale with MeOH–HCl gives Me glycyrrhetate (**I**), which is oxidised (CrO_3) to the *diketo-ester*, m.p. 238—240°, saponified and isomerised by N_2H_4–NaOEt to the *diketo-acid*, m.p. 325° (*Me* ester, m.p. 245—247°, not identical with the diketo-ester), and reduced (Zn–Hg–HCl–AcOH) to *Me deoxydeoxoglycyrrhetate*, m.p. 182°. Hydrolysis (KOH–H_2O–EtOH; 170°) of this ester affords the *acid*, m.p. 303—305°, unimol. films of which have a limiting area of only 46 sq. A.; the CO_2H must therefore be attached to a terminal ring of the hydropicene skeleton, viz., at $C_{(20)}$ in ring E, and the acid is epimeric with γ-oleananic acid. Boiling Ac_2O–NaOAc and (**I**) followed by Clemmensen reduction yield Me acetyldeoxyglycyrrhetate, which with boiling AcOH–SeO_2 gives *Me acetyldehydrodeoxoglycyrrhetate*, m.p. 230—231°, $[\alpha]_D$ −32° in $CHCl_3$, hydrolysed to *dehydrodeoxoglycyrrhetic acid*, m.p. >305° (*Me* ester, m.p. 262—263°), and having an absorption spectrum indistinguishable from that of Me acetyldehydro-oleanolate and of acetyldehydroamyrin. *Dehydro-oleanolic acid*, m.p. 274—275°, prepared by hydrolysis under pressure of the corresponding Me ester, gives on heating, with loss of CO_2, *oleadienol* I (+MeOH), m.p. 218—219°, $[\alpha]_D$ +97° in dioxan, containing two double bonds. Acetylketo-oleanolic acid (**II**) is decarboxylated in boiling quinoline to an acetoxy-ketone, m.p. 235—240°, and in a sealed tube at 340°, yields *oleadienone* II, m.p. 210—212°, reduced (Na–EtOH) to *oleadienol* II, m.p. 219—221°. This alcohol gives unimol. films of small area, indicating that the polar group, representing the CO of the parent acid, is situated in one of the end rings : this is compatible with the formula for (**II**), but not with previous structures assigned to oleanolic acid. *Norechinocystadienol acetate* has m.p. 175—177°, $[\alpha]_D$ +46° in dioxan.

XV. Siaresinolic acid (**III**) is shown to belong to the β-amyrin group of triterpene acids by its conversion into oleanene III (**IV**); one OH occupies a position at $C_{(2)}$ in ring A and the second OH is attached to $C_{(21)}$ in ring E, the double bond being in the βγ-position with regard to this C. Apart from the additional OH at $C_{(21)}$, (**III**) is identical with oleanolic acid and its reactions support the formula put forward in Part XIII. Me siaresinolate (**V**) with Ac_2O–C_5H_5N gives the *Ac* derivative, m.p. 110—120°, which is oxidised (CrO_3) to *Me acetyl*-21-*keto-oleanolate*, m.p. 232—234°, hydrolysed (KOH) and esterified (CH_2N_2) to the *β-hydroxy-keto-ester*, m.p. 189—190°, $[\alpha]_D$ −195°. Oxidation (CrO_3) of (**V**) affords *Me α-siaresinonate*, m.p. 210°, $[\alpha]_D$ +135°, saponified to the acid, m.p. 295° (decomp.), $[\alpha]_D$ −187°, re-esterified (CH_2N_2) to the *β-ester*, m.p. 190°, $[\alpha]_D$ −192°; the isomerisation is due to the wandering of the double bond during hydrolysis. Reduction (Zn–HCl–AcOH) of the α-ester gives *Me* 21-*ketodihydro-oleananate*, m.p. 200—201°, $[\alpha]_D$ +25·3°, only one CO group being attacked, and with N_2H_4–NaOEt, the ester forms β-deoxosiaresinonic acid, m.p. ~297° (decomp.) (*Me* ester, m.p. 214°, $[\alpha]_D$ −225°). This acid is decarboxylated to *norsiaresinone*, m.p. 237—238°, $[\alpha]_D$ +152° (*dione*, m.p. 290°), which is reduced by Zn–HCl to (**IV**) and with Na–EtOH to *dihydronorsiaresinol* (**VI**), m.p. 166—167°, and the *diene hydrocarbon*, m.p. 126—127°, $[\alpha]_D$ −33°. Me 2-acetylsiaresinolate is dehydrated (P_2O_5) to Me acetyldehydro-oleanolate. Surface film measurements of (**VI**) indicate that the second OH is at $C_{(21)}$. All rotations arc in $CHCl_3$.

XVI. α-Elemolic, m.p. 218—220°, $[\alpha]_D$ −24·7°, and β-elemonic acid, m.p. 212—214°, $[\alpha]_D$ +45°, have been separated from the resin by an improved method, using Girard's reagent. Both acids contain two double bonds, only one of which is reactive, and they are therefore tetracyclic. Reduction of acetyl-α-elemolic acid (PtO_2–H_2) gives the H_2-acid, m.p. 244—245°, $[\alpha]_D$ −33° (lit. 248·5° and −30·0°; *Me* ester, m.p. 135°). Me α-elemonate and N_2H_4–NaOEt afford *α-elemanic acid*, m.p. 257°, $[\alpha]_D$ −29° (*Me* ester, m.p. 131—132°), and with Zn–HCl–AcOH, *Me* iso-*α-elemanate*, m.p. 87° (*acid*, m.p. 257°, $[\alpha]_D$ −20°), is obtained. Dihydro-α-elemonic acid is prepared by hydrogenation of α-elemonic acid and an isomer [*oxime*,

m.p. 234—235° (decomp.)] is obtained from dihydro-α-elemolic acid and CrO_3. *Me dihydro-α-elemonate*, m.p. 172—174°, with N_2H_4–NaOEt gives *dihydro-α-elemanic acid*, m.p. 277—278°. Reduction (Zn–HCl–AcOH) of Me β-elemonate affords an *ester*, m.p. 82—83°, hydrolysed to *dihydro-β-elemanic acid* (**VII**), m.p. 258—259°, $[\alpha]_D$ +2°, re-esterified to the corresponding *Me* ester, m.p. 104—105°, whilst reduction with N_2H_4 yields a mixture of *β-elemanic acid* A, m.p. 224—226°, $[\alpha]_D$ +15°, and B, m.p. 216—217°, $[\alpha]_D$ +8·7°, both forming the same *Me* ester, m.p. 115—116°. β-Elemonic acid is reduced (PtO_2–H_2) to *dihydro-β-elemonic acid*, m.p. 237—238°, $[\alpha]_D$ +46·7° (*Me* ester, m.p. 112—113°), which with N_2H_4 gives (**VII**). α-Elemolic acid with HCO_2H–$CHCl_3$ gives a *compound*, $C_{30}H_{48}O_3,HCO_2H$, m.p. 225°, hydrolysed to the original acid, and the β-acid yields a *compound*, $C_{30}H_{46}O_3,HCO_2H,H_2O$, m.p. 223—224°, hydrogenated to an *acid*, m.p. 237°. Measurements of unimol. films of appropriate derivatives suggest that both α-elemolic and β-elemonic acids have the CO_2H at one end of the polycyclic system, whereas the remaining O is at the opposite end of the mol. The double bonds of the α-acid probably occupy βγ-positions with respect to each other. The work of Ruzicka *et al.* (A., 1933, 69) and Mladenovic *et al.* (A., 1932, 1253) is criticised. All rotations are in $CHCl_3$ unless it is otherwise stated. F. R. S.

VI.—HETEROCYCLIC.

Optical rotatory dispersion of (−)-tetrahydrofurfuryl alcohol.—See A., 1942, I, 388.

Furfuryl formate. W. R. Edwards, jun., and L. H. Reeves (*J. Amer. Chem. Soc.*, 1942, **64**, 1583—1584).—Addition of HCO·OAc to furfuryl alcohol and HCO_2Na at room temp. and subsequent heating at 60° gives 44% of *furfuryl formate*, m.p. <−68°, b.p. 166·3° (some decomp.)/760 mm., 66·2—66·5°/16 mm., which with H_2O_2 gives, *inter alia*, furfuraldehyde and HCO_2H, with *m*-$C_6H_4(NH_2)_2$ and HCl gives a resin, and does not promote growth of tomato leaves. Furfuryl oxalate could not be prepared. R. S. C.

Constitution of the coloured condensation product from furfuraldehyde, aniline, and aniline hydrochloride.—See A., 1942, II, 399.

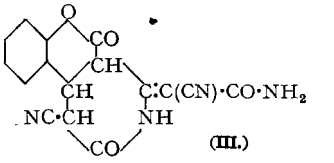
Hydantoins containing a tetrahydropyranyl substituent. H. R. Henze and R. L. McKee (*J. Amer. Chem. Soc.*, 1942, **64**, 1672—1674).—4-Cyanotetrahydropyran-4-carboxylic acid {prep. by way of the Et ester, b.p. 135°/16 mm., from CN·CH_2·CO_2Et, (Cl·$[CH_2]_2)_2$O, and NaOEt–EtOH at the b.p.}, m.p. 163—164° (lit. 160—162°), when heated at 180—200° gives 4-cyanotetrahydropyran, b.p. 82—83°/10 mm., converted by MgRHal and then aq. NH_4Cl or HCl into 4-tetrahydropyranyl Me, b.p. 205—207°/144 mm. (m.p. 178°, 160—161°; these and other data in parentheses refer to *semicarbazones* and 2 : 4-*dinitrophenylhydrazones*, respectively), Et, b.p. 101°/20 mm. (m.p. 151°, 146—147°), *Pr*$^{\alpha}$, b.p. 85—88°/5 mm. (m.p. 145—146°, —), Bu$^{\alpha}$, b.p. 100°/5 mm. (m.p. 180°, 99°), *Bu*$^{\beta}$, b.p. 90—92°/6 mm. (m.p. 187—188°, 122°), n-, b.p. 106—107°/5 mm. (m.p. 117°, 89—90°), and iso-*amyl*, b.p. 116—117°/7 mm. (m.p. 158—159°, 134—135°), n-*hexyl*, b.p. 134—135°/6 mm. (m.p. 161°, —), cyclo*hexyl*, b.p. 142°/5 mm. (m.p. 213—214°, —), and *Ph ketone*, m.p. 57—58°, which with KCN–$(NH_4)_2CO_3$ in 50% EtOH at 58—60° give 5-4′-*tetrahydropyranyl*-5-*methyl*-, m.p. 250°, -*ethyl*-, m.p. 246°, -n-*propyl*-, m.p. 223°, -n-, m.p. 195°, and -iso-*butyl*-, m.p. 222°, -n-, m.p. 171—172°, and -iso-*amyl*- (**I**), m.p. 195—196°, -n-*hexyl*-, m.p. 169°, -cyclo*hexyl*-, m.p. 304—306°, and -*phenylhydantoin* (**II**), m.p. 253°. (**I**) and (**II**) are mild anticonvulsants with no hypnotic effect. M.p. and b.p. are corr. R. S. C.

2-Carbobutoxy-6 : 6-dimethyl-5 : 6-dihydro-1 : 4-pyrones.—See B., 1942, II, 362.

Visible fluorescence and chemical constitution of the benzopyrone group. III. Structural influences in coumarins. V. Balaiah, T. R. Seshadri, and V. Venkateswarlu (*Proc. Indian Acad. Sci.*, 1942, **16, A**, 68—82; cf. A., 1941, II, 301).—The strong influence of CO, CN, and Ph in the 3- (but not the 4-)position in 7-hydroxycoumarins in enhancing fluorescence is discussed. In cases where the possibility of resonance initiated by CO is excluded; *e.g.*, in dihydroumbelliferone and its derivatives, no fluorescence is noted. The colour of visible fluorescence of 40 OH- and OMe-coumarins in H_2SO_4, EtOH, or dil. alkali is recorded. Amongst monohydroxycoumarins, the presence of OH in position 7 is most effective; at 6 a feeble effect exists, but at 3 and 8 no fluorescence is noted. With dihydroxycoumarins, the 6 : 7 derivatives show a greater fluorescence than the 5 : 7, but 8 : 7 compounds exhibit none. Higher polyhydroxy-derivatives give no fluorescence. Although 5-methoxycoumarin gives a feeble fluorescence, the 8-isomeride does not. Umbelliferone-3-acetic acid gives none, but the -4-carboxylic acid and 4-phenylumbelliferone show a feeble fluorescence. Several compounds, *e.g.*, 7-acetoxy- and -methoxy-3-phenylcoumarin, show fluorescence in the solid state. 2 : 4 : 1-$(OH)_2C_6H_3$·CHO–CN·CH_2·CO_2Et–piperidine give 7-*hydroxy*-3-*cyanocoumarin*, m.p. 262°. Orcylaldehyde and CH_2Ph·CO_2Na–Ac_2O at 170—180° yield 7-acetoxy- and thence 7-hydroxy-3-phenyl-5-methylcoumarin. 3-Methylresorcylaldehyde and CH_2Ac·CO_2Et or $CH_2(CO_2Et)_2$ + piperidine afford 7-*hydroxy*-3-*acetyl*-8-*methylcoumarin*, m.p. 256—257°, or *Et* 7-*hydroxy*-8-*methylcoumarin*-3-*carboxylate*, m.p. 250—251° (free *acid*, m.p. 277—278°), respectively. 7-*Hydroxy*-4-*phenyl*-8-*methylcoumarin*, m.p. 279—280°, is prepared from 2 : 1 : 3-$C_6H_3Me(OH)_2$–CH_2Bz·CO_2Et–H_2SO_4 at room temp., and 4 : 3 : 2 : 1-OMe·$C_6H_2Me(OH)$·CHO–CH_2Ac·CO_2Et–piperidine afford 7-*methoxy*-3-*acetyl*-8-*methylcoumarin*, m.p. 191—192°. 3 : 5 : 1 : 4 : 2-$(OMe)_2C_6H(OH)_2$·CHO and $CH_2(CO_2Et)_2$–piperidine yield *Et* 6-*hydroxy*-5 : 7-*dimethoxycoumarin*-3-*carboxylate*, m.p. 190° (free *acid*, m.p. 252°). 1 : 3 : 5-$C_6H_3(OH)_3$ and Et_2 acetosuccinate in H_2SO_4 at room temp. give *Et* 5 : 7-*dihydroxy*-4-*methylcoumarin*-3-*acetate*, m.p. 240° (corresponding *acid*, m.p. 264°). 7 : 8-*Dihydroxy*-4-*methyl*-, m.p. 277°, and 5-*hydroxy*-4 : 7-*dimethyl*-*coumarin*-3-*acetic acid*, m.p. 271°, are obtained by hydrolysing the corresponding Et esters. 5-*Benzyloxy*-4 : 7-*dimethylcoumarin*, m.p. 150°, is prepared from the 5-OH-compound by refluxing with CH_2PhCl–K_2CO_3–$COMe_2$. Methylation of the respective OH-compounds with MeI–K_2CO_3–$COMe_2$ affords 7-*methoxy*-4-*phenyl*-3 : 4-*dihydrocoumarin*, +0·5H_2O, m.p. 43—44°, 7-*methoxy*-3-*phenyl*-5-*methylcoumarin*, m.p. 155°, 5-*methoxy*-4 : 7-*dimethylcoumarin*-3-*acetic acid*, m.p. 225° (*Et* ester, m.p. 117°), 5 : 7-*dimethoxy*-3-*phenylcoumarin*, +H_2O, m.p. 179—180°, and 5 : 7-, m.p. 218—220° (*Et* ester, m.p. 134°), and 7 : 8-*dimethoxy*-4-*methylcoumarin*-3-*acetic acid*, m.p. 194° (*Et* ester, m.p. 87°). A. T. P.

Reactivity of the double linking in coumarins and related unsaturated carbonyl compounds. VIII. Addition of cyanoacetamide to umbelliferone and its methyl ether. T. R. Seshadri and V. Venkateswarlu (*Proc. Indian Acad. Sci.*, 1942, **15, A**, 424—428; cf. A., 1928, 298).—CN·CH_2·CO·NH_2 (**I**) and 7-methoxycoumarin (**II**), with EtOH + piperidine [1 c.c. to 2 g. of (**II**)], give, after boiling for 50 hr., 90% of 7-*methoxy*-3 : 4-*dihydrocoumarin*-4-*cyanoacetamide*, m.p. 262—263°, hydrolysed by cold HCl to the 4-*cyanoacetic acid*, m.p. 247—249°, further hydrolysed by boiling HCl to 7-*methoxy*-3 : 4-*dihydrocoumarin*-4-*acetic acid*, m.p. 122—123° (also obtained from 7-methoxycoumarin-4-acetic acid and Na–Hg in EtOH at 50—60° for 3 days). (**I**) and 7-hydroxycoumarin afford, similarly, after 120 hr., 90% of 7-*hydroxy*-3 : 4-*dihydrocoumarin*-4-*cyanoacetamide*, +0·5H_2O (does not melt at <300°), hydrolysed to 7-*hydroxy*-3 : 4-*dihydrocoumarin*-4-*acetic acid*, m.p. 180—181° (also obtained from 7-hydroxycoumarin-4-acetic acid). A. T. P.

Reactivity of the double linking in coumarins and related unsaturated carbonyl compounds. IX. Addition of cyanoacetamide to coumarins with electron-attracting groups in the 3-position. V. D. N. Sastry and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **16, A**, 29—35).—3-Acetyl- (**I**) or -benzoyl-coumarin and CN·CH_2·CO·NH_2 (**II**) in EtOH–piperidine (boil) give poor yields of 3-*acetyl*-, decomp. 295° (shrinks at 290°), or 3-*benzoyl*-*dihydrocoumarin*-4-*cyanoacetamide*, m.p. 315° (decomp.) (sinters at 308°), respectively. Et coumarin-3-carboxylate reacts with 2 mols. of (**II**) to give a *compound* [possibly (**III**) or similar type, *i.e.*, 5′-*cyano*-1-*keto*-2′-(*carbamylcyanomethylene*)-1′ : 2′ : 3′ : 4′ : 5′ : 6′-*hexahydrocoumarinopyrido*-3′ : 4′-3 : 4-*coumarin*], m.p. >360°, and the piperidide of coumarin-3-carboxylic acid (also obtained from the ester and piperidine in boiling PhMe). Coumarin-3-carboxylic acid reacts with (**II**) similarly to coumarin to give, with decarboxylation, 3 : 4-dihydrocoumarin-4-cyanoacetamide. 3-Cyanocoumarin (**IV**), m.p. 185—186°, and (**II**) afford 3-*cyanodihydrocoumarin*-4-*cyanoacetamide* (does not melt at <360°). (**I**) refluxed with EtOH + piperidine yields 3 : 4-*dihydro*-4 : 4′-*dicoumarinyl*, m.p. 293° (decomp.), and the same product results in presence of $CH_2(CO_2Et)_2$, CH_2Ac·CO_2Et, or CN·CH_2·CO_2Et. 3-Substituted coumarins do not react with the last-named reagents, with the exception of (**IV**), which with CN·CH_2·CO_2Et and piperidine gives *Et* 3-*cyanodihydrocoumarin*-4-*cyanoacetate*, m.p. 247—248° [also obtained from Et_2 salicylidenebiscyanoacetate (**V**), m.p. 140—141°, and EtOH–piperidine]. *o*-OH·C_6H_4·CHO–CN·CH_2·CO_2Et–piperidine at room temp. give (**IV**), but the use of 2 mols. of CN·CH_2·CO_2Et affords (**V**). A. T. P.


(III.)

Synthetic experiments in the benzopyrone series. V. Action of aluminium chloride on karanjin. B. Krishnaswamy and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **15, A**, 437—440; cf. A., 1941, II, 330).—Karanjin and $AlCl_3$–$PhNO_2$ at 80—85° afford karanjanol, m.p. 192—193°; the use of C_6H_6 or PhMe as solvent gives *α-phenyl*-, m.p. 260—262° (*Ac*$_1$ derivative, m.p. 138—139°; *Me ether*, m.p. 151—153°), or *α-tolyl*-*αβ-dihydrokaranjonol*, m.p. 274—276° (*Ac* derivative, m.p. 145—146°; *Me ether*, m.p. 157—159°), respectively. 7-Methoxy- (**I**), 7-hydroxy-3-methoxy- (**II**), and 3 : 7-dimethoxy-flavone (**III**) are readily demethylated by $AlCl_3$–C_6H_6; with $AlCl_3$ in $PhNO_2$, however, (**I**) is unaffected, (**II**) gives 3 : 7-dihydroxyflavone, and (**III**) yields 3-hydroxy-7-methoxyflavone, m.p. 177—178°. A. T. P.

Natural coumarins. LVIII. Dihydro-oreoselonic acid. E. Späth and A. Kleedorfer (*Ber.*, 1942, **75**, [*B*], 298—299; cf. *ibid.*, 1941,

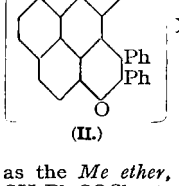
74, 1789).—In reply to von Bruchhausen *et al.* (A., 1942, II, 269) the authors maintain the accuracy of their determinations of m.p. in the dihydro-oreoselonic acid (**I**) series and of their observation that (**I**) passes into dihydro-oreoselone when sublimed in high vac. H. W.

Structure of α-nitrotetronic acid.—See A., 1942, 1, 388.

Anti-sterility factor (vitamin-*E*). XI. Synthetic α-tocopherol without phytol. W. John and H. Pini (*Z. physiol. Chem.*, 1942, **273**, 225—234).—Hexahydrofarnesyl bromide and KCN–EtOH afford the corresponding *nitrile*, b.p. 109—110°/0·4 mm., reduced (Na–EtOH) to δθμ-trimethyltridecylamine (**I**). The Bz derivative of (**I**) with PBr_5 or PCl_5 at 100° (bath), followed by thermal decomp. at 180—200°/0·3 mm. or 270—300°, respectively, and treatment with HCl–EtOH, yields *δθμ-trimethyltridecyl bromide* (**II**), b.p. 123—124°/0·4 mm., or *chloride* (**III**), b.p. 112°/0·4 mm., respectively. The Grignard reagent from (**II**) or (**III**) and 5 : 3 : 4 : 6 : 2 : 1-OAc·C_6Me_3(OMe)·$[CH_2]_2$·COMe in Et_2O–C_6H_6 afford a product which on successive treatment with boiling 5% KOH–MeOH (N_2), $FeCl_3$–EtOH, Zn–AcOH, and HBr (*d* 1·49)–AcOH–Zn yields *s*-α-tocopherol, purified through the allophanate (chromatographic separation), m.p. 175—176°. The derived di-*p*-bromobenzoate, m.p. 114°, of the α-tocopherylquinol does not depress the m.p. of the similar ester, m.p. 114—115°, from *dl*-α-tocopherylquinol (Karrer *et al.*, A., 1939, II, 335). A. T. P.

Anthochlor pigments. III. Pigments of *Cosmos sulphureus*. T. A. Geissman (*J. Amer. Chem. Soc.*, 1942, **64**, 1704—1707).—The rays of *C. sulphureus* yield the amorphous pentahydroxychalkone hexoside (termed *coreopsin*), +1·5H_2O, sinters at ~150°, decomp. 190—195°, previously obtained (A., 1942, III, 360) from *Coreopsis gigantea*. The acetate, m.p. 171—172°, thereof with HCl–H_2O–MeOH and then Ac_2O and NaOAc gives, by hydrolysis, ring-closure, and re-acetylation butin triacetate. The chalkone structure is shown by its colour (yellow alone; red in aq. NaOH) and lack of colour formation with Mg–HCl. The (unidentified) sugar is probably attached at the 2- or 4-position. The disc-florets and bracts contain a quercitin glucoside (? *iso*quercitrin) and luteolin (free; isolated as acetate). The relations of the constituents is discussed. R. S. C.

Dehydrenium. IV. Dehydrenium salts of the benzochromenium series and dehydrobenzo-α-chromone. W. Dilthey and H. Giebert (*Ber.*, 1942, **75**, [*B*], 211—215; cf. A., 1939, II, 223, 224).—MgPhBr and 3 : 4-diphenyl-5 : 6-benzochromone (**I**) give 2 : 3 : 4-triphenylbenzochromanol, m.p. 105—107°, the *perchlorate*, m.p. 245—246° (decomp.), of which is transformed by prolonged irradiation in boiling AcOH into *dehydro*-2 : 3 : 4-*triphenylbenzochromenium perchlorate* (**II**), m.p. 280—282°, characterised by its darker colour, more pronounced fluorescence, and greater stability. The possibility that dehydrogenation occurs between the Ph groups at $C_{(2)}$ and $C_{(3)}$ appears excluded since 2 : 3-*diphenylbenzochromenium perchlorate*, m.p. 272—274° (decomp.), obtained from 2 : 1-OH·$C_{10}H_6$·CHO and COPh·CH_2Ph in Et_2O containing HCl and $HClO_4$, could not be dehydrogenated; it is transformed by $NaHCO_3$ in warm $COMe_2$ into the *carbinol*, m.p. 151°, analysed as the *Me ether*, m.p. 110°. 1 : 2-$C_{10}H_6$Bz·OH is transformed by CH_2Ph·COCl at 100° or in boiling $COMe_2$ or PhMe containing anhyd. K_2CO_3 into (**I**), which is readily converted by $AlCl_3$–NaCl at 230° or by protracted insolation in 85% H_2SO_4 into *didehydro*-3 : 4-*diphenyl*-5 : 6-*benzo*-α-*chromone*, m.p. 317—318°. *Dehydro*-3 : 4-*diphenyl*-5 : 6-*benzo*-α-*chromone*, m.p. 266—267°, obtained from 4-hydroxybenzanthrone and CH_2Ph·COCl at 200—230°, could not be caused to react with MgPhBr or dehydrogenated. 2 : 3-*Diphenyl*-5 : 6-*benzopyrenium perchlorate*, m.p. 251—253° (decomp.), obtained from *o*-OH·C_6H_4·CHO and COPh·CH_2Ph in MeOH saturated with HCl, is reduced by Zn dust and AcOH–fuming HCl to 2 : 3-*diphenyl*-5 : 6-*benzopyran*, m.p. 178—179°. H. W.



(II.)

2-Hydroxymethyl-1 : 3-dioxolan and other dioxolans.—See B., 1942, II, 362.

Reductive cleavage of dioxolones by the Grignard reagent. R. C. Fuson and A. I. Rachlin (*J. Amer. Chem. Soc.*, 1942, **64**, 1567—1571).—CMe_2 derivatives of α-OH-acids (prep. by $COMe_2$ and conc. H_2SO_4 at −10°) are reduced by $MgBu^{\gamma}Cl$ in Et_2O, but not by other Grignard reagents, MgI, $Al(OPr^{\beta})_3$, Zn–Cu, H_2–Pt or –Cu chromite, to the Pr^{β} ethers of the OH-acid. *E.g.*, 5-phenyl-2 : 2-dimethyl-1 : 3-dioxol-4-one (**I**), m.p. 45°, gives α-iso*propoxyphenylacetic acid* [*mandelic acid Pr^{β} ether*], m.p. 58—59° (p-*phenylphenacyl* ester, m.p. 114—115°), also obtained by treating CHPhCl·COCl with EtOH and then NaOPr^{β}–Pr^{β}OH at 100°. 5-p-*Tolyl*-, m.p. 56—57°, 5-p-*bromophenyl*-, m.p. 65—66°, and 5-*mesityl*-2 : 2-*dimethyl*-1 : 3-*dioxol*-4-*one*, m.p. 92°, 2 : 2 : 5-tri-, b.p. 58—60°/18 mm., and 2 : 2 : 5 : 5-*tetra-methyl*-1 : 3-*dioxol*-4-*one*, b.p. 71°/42 mm., give similarly α-*iso*propoxy-*p*-tolyl-, an oil (p-*phenylphenacyl* ester, m.p. 93—94°), -*p*-bromophenyl-, an oil (p-*phenylphenacyl* ester, m.p. 90—91°), and -*mesityl-acetic*, m.p. 83—84°, α-iso*propoxy-propionic*, b.p. 72—75°/2 mm., and -iso*butyric acid*, b.p. 102—103°/15 mm. (p-*phenylphenacyl* ester, m.p. 88°), respectively. *o*-C_6H_4Me·MgBr and (**I**) in Et_2O at room temp. and later the b.p. give α-*phenyl*-ββ-*di*-o-*tolylethylene glycol* (**II**), m.p. 146° (2 active H), with small amounts of 5-*phenyl*-4 : 4-*di*-o-*tolyl*-2 : 2 -*dimethyl*-1 : 3-*dioxolan* (**III**), m.p. 108—109°, and *Ph di*-o-*tolylmethyl ketone* (**IV**), m.p. 104—106°. With $COMe_2$–H_2SO_4 at room temp. (**II**) gives (**I**), with Ac_2O–C_5H_5N gives the α-*acetate* (**V**), m.p. 158—160° (1 active H), and with conc. HCl (3 drops) or *p*-C_6H_4Me·SO_3H (a little) in boiling Ac_2O gives α-*acetoxy*-α-*phenyl*-ββ-*di*-o-*tolylethylene*, m.p. 138·5—140° [also obtained from (**V**) by AcCl or (**IV**) by Ac_2O–C_5H_5N]. Conc. HCl (3 drops) in boiling MeOH, HI, 30% H_2SO_4, H_3PO_4, or *p*-C_6H_4Me·SO_3H converts (**I**), and HCl or *p*-C_6H_4Me·SO_3H converts (**II**), into (**IV**). (*o*-C_6H_4Me)$_2$CH·OH (prep. from *o*-C_6H_4Me·MgBr by HCO_2Et in Et_2O) gives the chloride and thence by CuCN–C_5H_5N at 200—215° into *di*-o-*tolylacetonitrile* (54%), m.p. 114—115°, which with MgPhBr–Et_2O and then aq. HCl at 100° gives (**IV**). R. S. C.

Preparation of deuterium derivatives of pyrrole. F. A. Miller (*J. Amer. Chem. Soc.*, 1942, **64**, 1543—1544).—1-Deuteropyrrole is prepared from K pyrrole by 99·6% D_2O in Et_2O and by shaking pyrrole with D_2O at p_H ≮2. The latter method at p_H 1 (obtained by adding DCl) gives penta-, which with H_2O at p_H 7 gives 2 : 3 : 4 : 5-tetradeuteropyrrole. Structures and purity (≮99% attained) are determined by Raman spectra. R. S. C.

Preparation of certain 2-thiolpyridine derivatives. M. A. Phillips and H. Shapiro (*J.C.S.*, 1942, 584).—By using the appropriate halogenopyridine and $CS(NH_2)_2$, thiolpyridines are prepared: 2-(5-*nitropyridyl*)iso*thiocarbamide hydrochloride*, m.p. 191° (decomp.), is reduced to 2-(5-*aminopyridyl*)iso*thiocarbamide dihydrochloride* (+H_2O), m.p. 204° (decomp.). F. R. S.

Esters of pyridinecarboxylic acids as local anæsthetics. F. F. Blicke and E. L. Jenner (*J. Amer. Chem. Soc.*, 1942, **64**, 1721—1724).—Pyridine-3-carboxyl chloride and the appropriate OH-amine in boiling $Pr^{\beta}OH$ or the acid and the NR_2-alkyl chloride in C_6H_6 give β-*diethylaminoethyl*, m.p. 127—128° (A., 1926, 2445, m.p. 140—160°) (free base, b.p. 120—125°/2 mm.), -*di*-n-*butylamino*-n-*propyl*, m.p. 104—105°, β-*dicyclohexylaminoethyl*, m.p. 163—165°, and γ-*diethylamino*-α-*phenyl*-n-*propyl*, m.p. 145—146°, *pyridine*-3-*carboxylate hydrochloride*. Quinolinic anhydride (modified prep.) with boiling ROH (excess or in PhMe) gives Me, m.p. 125—126° (lit. 123°), n-*amyl*, m.p. 110—111°, n-*octyl*, m.p. 104—105°, n-*dodecyl*, m.p. 106—107°, and β-*phenylethyl*, m.p. 139—140°, *pyridine*-2-*carboxylate*-3-*carboxylic acid*. The derived acid chloride with the NR_2-alkyl chloride in $Pr^{\beta}OH$ gives 2-Me (*hydrochloride*, m.p. 113—114°), 2-*n*-amyl (*hydrobromide*, m.p. 98—101°), 2-*n*-octyl (*hydrobromide*, hygroscopic, m.p. 59—62°), 2-*n*-dodecyl (*hydrobromide*, m.p. 72—74°), and β-phenylethyl 3-β-diethylaminoethyl pyridine-2 : 3-dicarboxylate (*hydrochloride*, m.p. 141—142°), and 2-*n*-amyl 3-γ-di-*n*-butylamino-*n*-propyl pyridine-2 : 3-dicarboxylate (*hydrochloride*, an oil). *Di*-β-*diethylaminoethyl pyridine*-2 : 3-*dicarboxylate dihydrobromide* has m.p. 157—159°. γ-Diethylamino-α-phenyl-*n*-propyl (prep. from the NH_2-ketone hydrochloride by H_2–Raney Ni in H_2O at 3 atm.), b.p. 122—124°/2 mm. (*hydrochloride*, m.p. 84—86°), and *dicyclo*hexylaminoethyl alcohol (prep. from the *sec.* amine and Br·$[CH_2]_2$·OH at 100°), b.p. 131—134°/2 mm., are described. The esters have no or slight local anæsthetic activity. R. S. C.

Synthesis of the three isomeric *dl*-β-pyridylalanines. C. Niemann, R. N. Lewis, and J. T. Hays (*J. Amer. Chem. Soc.*, 1942, **64**, 1678—1682).—2-Pyridylmethylamine with, successively, $NaNO_2$–HCl–H_2O, KOH, NHBz·$CH(CO_2Et)_2$–NaOEt–EtOH, and boiling 49% HBr gives *dl*-β-2-pyridylalanine (**I**) (17%), m.p. 205·5—206° (lit. 216°). $BzSO_2Cl$ and pyridine-4-carboxylhydrazide in C_5H_5N give *pyridine*-4-*carboxylbenzenesulphonhydrazide*, m.p. 202—203·5°, converted by Na_2CO_3 in glycerol at 160° into pyridine-4-aldehyde [phenylhydrazone hydrochloride, m.p. 194·5—197° (lit. 196°)]. Similarly are prepared *nicotinoylbenzenesulphonhydrazide*, m.p. 186—186·5°, and nicotinaldehyde (**II**), b.p. 97—99°/26 mm. (phenylhydrazone, m.p. 157·5—158°), which with acetylthiohydantoin and NaOAc in Ac_2O at 110—115° gives 5-3′-*pyridylmethylthiohydantoin*, m.p. 249—252°. Diketopiperazine, (**II**), and NaOAc in Ac_2O at 120—125° give *dinicotinylidenediketopiperazine*, m.p. >300°, converted by boiling red P–HI–Ac_2O into dl-β-3-*pyridylalanine* (**III**), m.p. 262—263° (*picrate*, m.p. 187—189°). *iso*Nicotinhydrazide, m.p. 170·5—171·5° (lit. 163°), gives the *$PhSO_2$* derivative, m.p. 193—194°, which does not yield the aldehyde. 4-*Hydroxymethylpyridine hydrochloride* (prep. from the amine by $AgNO_2$ etc.), m.p. 167—172°, with boiling 49% HBr gives 4-*pyridylmethyl bromide hydrobromide*, m.p. 145—150°, converted by NHBz·$CH(CO_2Et)_2$–Na–PhMe (or –EtOH) into a condensation product, m.p. 106—107°, which by hydrolysis yields dl-β-4-*pyridylalanine* (**IV**), m.p. 235—236°. Other attempts to prepare (**III**) and (**IV**) failed. $k_{B_1} \times 10^{10}$, $k_{B_2} \times 10^{12}$, and $k_A \times 10^{10}$ are (**I**) 0·89±0·05, 2±1, 6±1, (**III**) 3·7±0·5, 5±1, 8±1, and (**IV**) 6±1, —, —, respectively. R. S. C.

Substituted 5-aminopyridine-2-sulphonamides. W. T. Caldwell and E. C. Kornfeld (*J. Amer. Chem. Soc.*, 1942, **64**, 1695—1698).—

5-NO_2 activates the 2-position of C_5H_5N. 2-Aminopyridine and H_2SO_4–HNO_3 (*d* 1·49) at 40—45° and then room temp. give the 5- (+7% of 3-)NO_2-derivative, converted by H_2SO_4–HNO_3 at 10—15° and then the b.p. into 5-nitro-2-pyridone (59%). PCl_5–$POCl_3$ then gives 2-chloro-5-nitropyridine (90—95%), m.p. 107—108°, which with boiling aq. Na_2SO_3 gives 5-nitro-2-methoxypyridine and with $CS(NH_2)_2$ gives 5-nitro-2-pyridyl-ψ-thiocarbamide hydrochloride (85%), converted by aq. Na_2CO_3–NaOH into 5-nitro-2-thiolpyridine (80—83%), m.p. 188—191° (decomp.) (and a little di-5-nitro-2-pyridyl sulphide). With $Na_2S_2O_4$ and then Ac_2O in H_2O at <50° this gives *5-acetamido-2-thiolpyridine* (**I**) (40—45%), m.p. 244—246°, which with warm aq. 30% H_2O_2 gives *di-5-acetamido-2-pyridyl disulphide* (90%), m.p. 240—241°, but with 30% H_2O_2 in AcOH at <70° gives *5-acetamidopyridine-2-sulphonic acid* (**II**) (82%), m.p. 302—303° (decomp.) (S-*benzylthiuronium* salt, m.p. 93—95°), and thence (aq. $Na_2S_2O_4$; then Ac_2O) *5-acetamido-2-pyridone*, m.p. 232—233°. *5-Acetamidopyridine-2-sulphonyl chloride*, m.p. 165—166° (decomp.), is obtained (85%) from (**I**) by Cl_2–H_2O–HCl but not from (**II**) by any method. With NH_3, NH_2R, etc., usually in C_5H_5N at 60°, and then 0·5—1N-NaOH (or HCl), this gives *5-aminopyridine-2-sulphon-amide*, m.p. 184—185° [N^5-*Ac* derivative, m.p. 231—233° (decomp.)], *-amidopyridine*, m.p. 205—206° (decomp.) [N^5-*Ac* derivative, m.p. 231—232° (decomp.)], *-anilide*, m.p. 164—165° (N^5-*Ac* derivative, m.p. 213—214°), *-guanidide*, m.p. 220—221° (decomp.) [N^5-*Ac* derivative, m.p. 228—229° (decomp.)], *-amidothiazole*, m.p. 226—227° (decomp.) [N^5-*Ac* derivative, m.p. 234—235° (decomp.)], *-amidopiperazine*, m.p. 283—285° (decomp.) [N^5-*Ac* derivative, m.p. 231—232° (decomp.)], and *-amidoiodopyridine*, m.p. 219—220° (decomp.) [N^5-*Ac* derivative, m.p. 225—226° (decomp.)]. M.p. are corr. R. S. C.

Syntheses by means of magnesylindoles. Series II. XXVIII. Thio-derivatives of indoles. B. Oddo and (Signa.) L. Raffa (*Gazzetta*, 1941, **71**, 242—253).—The product from 2-methylindole (**I**), Mg, and EtBr heated at 100° with S (washed with aq. NH_3 and dried), followed by AcCl, gives the 3-Ac derivative of (**I**), and *3-acetylthiol-2-methylindole*, m.p. 311—312°. Using BzCl, the products are the 3-Bz derivative of (**I**), and *3-benzoylthiol-2-methylindole*, m.p. 237—238° (decomp.). The Mg derivative from skatole with S, followed by ice and CO_2, gives 3 : 3′-*dimethyl*-2 : 2′-*di-indolyl trisulphide*, m.p. 145° (decomp. 155°) [*Ag* derivative, decomp. 140°; *dipicrate*, m.p. 152° (explodes 160°)], or with S followed by BzCl, *2-benzoylthiol-3-methylindole* (**II**), m.p. 90—100° (decomp. 162°) [*Ag* derivative, m.p. 250° (decomp. from 125°)], and a product, m.p. 135—136°. Hydrolysis of (**II**) gives a product, m.p. 190—196° (decomp., softens at 165°), and KOH fusion gives *o*-NHAc·C_6H_4·CO_2H. E. W. W.

Indole polysulphides. (Signa.) L. Raffa (*Gazzetta*, 1941, **71**, 253—262).—2-Methylindole and S (washed with aq. NH_3 and dried) at 115—125° give H_2S and 2 : 2′-*dimethyl*-3 : 3′-*di-indolyl trisulphide* (**I**), m.p. 201° (decomp. 225—230°) (*Ag* derivative), which with Na_2S in $COMe_2$ gives the corresponding *disulphide* (**II**), m.p. 230°, also obtained from (**I**) in boiling 0·5N-NaOH–EtOH, or in cold BzCl (C_5H_5N), which at 100° (bath) with (**I**) or (**II**) gives the Bz_2 derivative, m.p. 100—105° (decomp.), of (**II**). E. W. W.

Reaction of magnesium phenyl bromide with 1-phenylisatin. W. C. Sumpter (*J. Amer. Chem. Soc.*, 1942, **64**, 1736—1737).—1-Phenylisatin and MgPhBr in boiling Et_2O give 1 : 3 : 3-*triphenyloxindole* (**I**), m.p. 161°, and 2 : 3-*epoxy*-1 : 2 : 3-*triphenylindole*, m.p. 238° (cf. Stollé *et al.*, A., 1933, 283; Myers *et al.*, A., 1939, II, 457). (**I**) is also obtained from 3 : 3-dichloro-1-phenyloxindole by $AlCl_3$–C_6H_6 at 60° and with PCl_5 at 150° gives 2 : 2-*dichloro*-1 : 3 : 3-*triphenyl*-2 : 3-*dihydroindole*, m.p. 200°. R. S. C.

Synthesis of keto- and mercapto-derivatives of cinchonic acid from rhodanine-oxindoles. R. V. Jones and H. R. Henze (*J. Amer. Chem. Soc.*, 1942, **64**, 1669—1672).—Rhodanine, the appropriate methylisatin, NaOAc, and a little Ac_2O in AcOH at 140° give *rhodanine-*$\Delta^{5:3'}$*-1-methyl-* (**I**), *-5′-methyl-* (**II**), and *-1′ : 5′-dimethyl-oxindole* (**III**) (also obtained by $NHEt_2$ as catalyst), m.p. >300°. With hot KOH–Me_2SO_4–EtOH, rhodanine-$\Delta^{5:3'}$-oxindole (**IV**) (A., 1929, 195) gives only 2-*keto*-3-*methylthiol*-1 : 2-*dihydrocinchonic acid* (**V**), m.p. 216—217° (decomp.), but with an excess gives 2-keto-1 : 2-dihydrocinchonic acid (**VI**). With 1 mol. of KOH in hot EtOH, (**IV**) gives a K_1 salt, which resists methylation or hydrolysis to oxindole; with 3 mols. of KOH, (**IV**) gives the K_2 salt of 2-keto-3-thiol-1 : 2-dihydrocinchonic acid, converted by AcOH into (**VI**) and S. (**I**), (**II**), and (**III**) are more readily hydrolysed: (**I**) gives the K_2 salt of 2-keto-3-thiol-1-methyl-1 : 2-dihydrocinchonic acid, m.p. variable, 145° (decomp.; corr.); (**II**) gives its K_1 salt or, if heated, the K_2 salt of 2-*keto*-3-*thiol*-6-*methyl*-1 : 2-*dihydrocinchonic acid*, m.p. 193—196° (decomp.; corr.) [S-CH_2Ph derivative, m.p. >200° (decomp.)], which with CH_2Cl·CO_2H in boiling H_2O gives 2-*keto*-6-*methyl*-1 : 2-*dihydrocinchonic acid*, m.p. 235—236° (decomp.), and S; (**III**) and alkali give the K_2 salt of 2-*keto*-3-*thiol*-1 : 6-*dimethylcinchonic acid*, m.p. 157—159° (decomp.; corr.). The K_2 salts with Me_2SO_4–H_2O at 0° and then 20% KOH give 2-*keto*-3-*methylthiol*-1 : 2-*dihydrocinchonic acid* (**VII**), m.p. 219—220° (decomp.; corr.) (*K* salt), -1- (**VIII**), m.p. 229—230° (decomp.; corr.), and -6-*methyl*-1 : 2-*dihydrocinchonic acid* (**IX**), m.p. 221—222° (decomp.; corr.) (*K* salt), and -1 : 6-*dimethyl*-1 : 2-*dihydrocinchonic acid* (**X**), m.p. 224—225° (decomp.; corr.) (*K* salt). Red P–HI at 150° converts (**VI**) into 2-keto-1 : 2 : 3 : 4-tetrahydrocinchonic acid, m.p. 215—216° (corr.), or (**VIII**) into an oil; HI at 150° converts (**IX**) into 2-keto-6-methyl-1 : 2 : 3 : 4-tetrahydrocinchonic acid, m.p. 219—220° (corr.); (**X**) gives only oils. R. S. C.

Sulphanilamido-derivatives of nitrogenous bases from Californian petroleum. L. M. Schenck and H. R. Henze (*J. Amer. Chem. Soc.*, 1942, **64**, 1499—1501).—In EtOH H_2–Raney Ni at 70°/1000 lb. (better than $SnCl_2$) reduces 5-nitro-, m.p. 124°, to 5-amino-2 : 3 : 8-trimethylquinoline, m.p. 110—111°, which in C_5H_5N yields 5-N^4-*acetylsulphanilamido-*, m.p. 260·5—261·5°, and thence (boiling 4N-HCl) 5-*sulphanilamido*-2 : 3 : 8-*trimethylquinoline* (**I**), m.p. 225·5—226°. Similarly are prepared 5-*amino-*, m.p. 101—102°, and 5-*sulphanilamido*-2 : 3-*dimethyl*-8-*ethylquinoline* (**II**), m.p. 241—242° (N^4-*Ac* derivative, m.p. 244—245°), 5-*amino-*, m.p. 90—92°, and 5-*sulphanilamido*-2 : 3-*dimethyl*-8-n-*propylquinoline* (**III**), m.p. 237—238° [N^4-*Ac* derivative (**IV**), m.p. 208—209°]. 5-*Nitro*-2 : 3-*dimethyl*-8-*ethyl-*, m.p. 107—109°, and -n-*propyl-quinoline*, m.p. 97—99°, are prepared from the base by HNO_3 (*d* 1·49) at 100°. M.p. are corr. (**I**), (**II**), and (**III**) have slight effect against hæmolytic streptococci but none against type I pneumococcus, *Staph. aureus*, or *Strep. viridans* in mice. (**I**), but not (**IV**), is active in 50-mg. doses in the blood against avian malaria, but 100-mg. doses of (**I**) are ineffective in the tissue. R. S. C.

Hydroxyquinolines. VI. Amino-derivatives of 8-hydroxy-7-benzylquinoline: 8-hydroxy-7-α-anilinobenzylquinoline. F. Pirrone (*Gazzetta*, 1941, **71**, 320—326).—8-Hydroxyquinoline heated with PhCHO and NH_2Ph, or with CHPh:NPh, gives 8-*hydroxy*-7-α-*anilinobenzylquinoline*, m.p. 146—147° (*picrate*, m.p. 142—143°; *dihydrochloride*, m.p. 122—124°; *formyl*, m.p. 220—225°, *Ac*, m.p. 203—204°, and *Bz*, m.p. 257—259°, derivatives; 5-*sulphonic acid*), which could not be converted into a quinoxazine. E. W. W.

Graebe–Ullmann synthesis of carbazole derivatives. Preparation and synthesis of 1-nitrocarbazole. R. W. G. Preston, S. H. Tucker, and (in part) J. M. L. Cameron (*J.C.S.*, 1942, 500—504).—Reduction of 2 : 4 : 1-$(NO_2)_2C_6H_3$·NHPh gives 4 : 2 : 1-NO_2·$C_6H_3(NH_2)$·NHPh, which with $NaNO_2$ (excess) in hot AcOH yields 5-nitro-1-phenyl-1 : 2 : 3-benztriazole. Careful pyrolysis thereof gives only a trace of 3-nitrocarbazole. *p*-C_6H_4Br·COMe is unchanged by HNO_3 (*d* 1·50) at 0°, but at higher temp. gives 4-*bromo*-3 : 5-*dinitroacetophenone*, m.p. 175—176°; with HNO_3 (*d* 1·52) at 0° it gives 3 : 4 : 1-NO_2·C_6H_3Br·COMe, which with NH_2Ph and K_2CO_3 gives 2 : 1 : 4-NO_2·C_6H_3(NHPh)·COMe; successive reduction ($SnCl_2$–HCl–AcOH), diazotisation, and pyrolysis (22% yield) then gives 3-acetylcarbazole. 2 : 4 : 1-NO_2·C_6H_3(CN)·NHPh (prep. from 3 : 4 : 1-NO_2·C_6H_3Cl·CN and NH_2Ph at the b.p.) by reduction (78%), diazotisation (65%), and pyrolysis (35%) gives 3-*cyanocarbazole*, m.p. 184—185°, which is also obtained from carbazole by condensation with CCl_3·CN and subsequent treatment with NH_3–PhCl and later KOH. The latter reaction with CCl_3·CN (2·4 mols.) and $AlCl_3$ in PhCl etc. gives similarly 3 : 6-*dicyanocarbazole*, m.p. >360°. 2 : 6 : 1-$(NO_2)_2C_6H_3$·NHPh (**I**) [prep. from 1 : 2 : 6-$C_6H_3Cl(NO_2)_2$ and NH_2Ph at 100° and later the b.p.] with H_2S–NH_3–H_2O gives 6 : 2 : 1-NO_2·$C_6H_3(NH_2)$·NHPh and thence 7-nitro-1-phenyl-1 : 2 : 3-benztriazole, m.p. 152°, which, when boiled with a little Cu-bronze, yields 18% of 1-*nitrocarbazole* (**II**). 2 : 6 : 4 : 1-$(NO_2)_2C_6H_2(CO_2H)$·NHPh [prep. from 3 : 5 : 4 : 1-$(NH_2)_2C_6H_2Cl$·CO_2H and NH_2Ph in boiling EtOH] with Cu in boiling quinoline gives (?) 1-*nitrophenazine*, m.p. 192—195°, and 11% of (**I**), and with Na_2S–S in NaOH–aq. EtOH gives 6 : 4 : 2 : 1-NO_2·$C_6H_2(NH_2)(CO_2H)$·NHPh, m.p. 239°, and thence 7-nitro-1-phenyl-1 : 2 : 3-benztriazole-5-carboxylic acid, which does not yield (**II**). With HNO_3 (*d* 1·42) in AcOH at 80°, carbazole gives the 3-(~70%), and 1-NO_2- (**III**) (6%; also obtained in similar yield by fuming HNO_3 in Ac_2O at 10—15°) and 3 : 6-$(NO_2)_2$-derivative (a little). Indefinite products are obtained by nitrating 9-acetylcarbazole. Addition of Ac_2O to (**III**) and KOH in hot $COMe_2$ gives 1-*nitro*-9-*acetylcarbazole*, m.p. 172—174°. 3 : 6-Bistrichloroacetylcarbazole (**IV**) (prep. described), m.p. 193—195°, and conc. HNO_3 in boiling AcOH give the 1-NO_2-derivative (**V**), m.p. 247—249°, and a substance which in boiling AcOH gives nitrous fumes and a *substance*, $C_{14}H_7O_7N_3$, m.p. >300°. In boiling dil. KOH, (**V**) gives $CHCl_3$ and 1-*nitrocarbazole*-3 : 6-*dicarboxylic acid* (**VI**), m.p. >300°, which with Cu-bronze in boiling quinoline gives (**I**) (38%). NaOEt–EtOH converts (**IV**) into Et_2 carbazole-3 : 6-dicarboxylate (**VII**) (67%), m.p. 206° (corr.), and a small amount of the acid. Et carbazole-3-carboxylate, m.p. 165—167°, is similarly (80%) prepared. Conc. HNO_3 in boiling AcOH converts (**VII**) into Et_2 1-*nitrocarbazole*-3 : 6-*dicarboxylate* (90%), m.p. 257—261°, hydrolysed (KOH–H_2O–EtOH) to (**VI**). Prep. of 9-*p*-toluenesulphonyl-, m.p. 127—128°, 3-*nitro*-9-p-*toluenesulphonyl-*, m.p. 208—211°, and 9-2′-*nitrotoluene*-4-*sulphonyl-carbazole*, m.p. 164°, is described. R. S. C.

Preparation of 1-substituted carbazoles. N. Campbell and J. A. R. MacLean (*J.C.S.*, 1942, 504—505).—1 : 3 : 4 : 5-$C_6H_2MeBr_2$·NO_2 (**I**) cannot be caused to react with $NHPh_2$ although with piperidine at

50° it gives piperidine hydrobromide. 5 : 3 : 4 : 1-NO_2·$C_6H_2Br_2$·CO_2H [best (30%) prepared from (**I**) by boiling HNO_3 (*d* 1·2)] with boiling NH_2Ph gives *2-bromo-6-nitrodiphenylamine-4-carboxylic acid*, m.p. 207—208° (*Me* ester, m.p. 151—152°, similarly prepared from the Me ester), which with aq. Na_2S at 100° gives *2-bromo-6-aminodiphenylamine-4-carboxylic acid*, m.p. 244—245° (*Ac* derivative, m.p. 163—164°). Diazotisation then gives *7-bromo-1-phenyl-1 : 2 : 3-benztriazole-5-carboxylic acid* (~100%), m.p. 215—217°, which with CaO at 360° gives as sole product a little carbazole (**II**). *2-Chloro-2'-nitrodiphenylamine*, m.p. 114°, is obtained (20%) from *o*-C_6H_4Br·NO_2, *o*-C_6H_4Cl·NH_2, K_2CO_3, and a little Cu-bronze at 160—170°. 3 : 6-Dibromo-1-aminocarbazole (Ac derivative, m.p. 262—264°) with boiling red P–HI gives 1-aminocarbazole (30%), converted by CH_2Br·COBr in boiling C_6H_6 into *1-ω-bromoacetamidocarbazole*, m.p. 188°, which in boiling KOH–EtOH gives a poor yield of the *lactam* [termed 2'-ketopiperazino(6' : 4' : 1 : 9)carbazole], m.p. 255°, of 1-aminocarbazole-9-acetic acid. Only (**II**) is obtained from 3 : 6-di-bromo- (**III**) or -iodo- or 1 : 3 : 6-tribromo-carbazole (**IV**) by red P–HI or from (**III**) (~100%) or (**IV**) (poor yield) by $SnCl_2$–conc. HCl–AcOH. Mecke's reagent gives colours with many derivatives of (**II**) or $NHPh_2$ as well as with phenols. Bromocarbazoles are readily identified by their fluorescence colours (ultraviolet). R. S. C.

Nitration of 9-*p*-toluenesulphonylcarbazole. B. K. Menon, E. V. Menon, and D. H. Peacock (*J.C.S.*, 1942, 509—510).—9-*p*-Toluenesulphonylcarbazole (**I**) (modified prep.), m.p. 137—138°, and 98% HNO_3 in AcOH at 60° give *1-nitro-9-p-toluenesulphonyl-* (**II**), m.p. 134°, hydrolysed by conc. HCl at 120—140° (not other methods) to 1-nitro-carbazole, new m.p. 187—188°. Boiling conc. HCl–EtOH–Sn reduces (**II**) to 1-amino-9-*p*-toluenesulphonylcarbazole, m.p. 134° [*Ac*, m.p. 8·8°, *Bz*, m.p. 165°, and derived 1 : 9-(p-C_6H_4Me·SO_2)$_2$ derivative, m.p. 241°], stable to HCl and 50% H_2SO_4. Br–AcOH at 60° and later 70° converts (**I**) into *3-bromo-9-p-toluenesulphonylcarbazole*, m.p. 148°, also obtained from 3-bromocarbazole. 98% HNO_3 in AcOH at 70°, later rising to 80—85°, converts (**I**) into two *dinitro-9-p-toluenesulphonylcarbazoles*, m.p. 271° and 207°, respectively, both obtained similarly also from (**II**). *3-Nitro-9-p-toluenesulphonylcarbazole* (**III**), m.p. 211°, is obtained from 3-nitrocarbazole and with HNO_3–AcOH–Ac_2O gives (?) 3 : 6-*dinitro-9-p-toluenesulphonylcarbazole*, m.p. 304°, also obtained (m.p. 302—303°) from 3 : 6-dinitrocarbazole. (**II**) is nitrated more rapidly than (**III**). 9-Ethyl-, -methyl-, and -benzyl-carbazolesulphonic acid and 2-*m*-carboxybenzenesulphonyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline resist resolution. R. S. C.

Syntheses of aminoacridines. II. 2 : 5-Diamino-7-ethoxyacridine, the base of "rivanol." A. Albert and W. Gledhill (*J.S.C.I.*, 1942, **61**, 159—160; cf. A., 1941, II, 232).—A practical method for making 2 : 5-diamino-7-ethoxyacridine, m.p. 226° (lit., 124—125°), of which "rivanol" is the lactate, is now described. The prep. of 2 : 5-diaminoacridine is improved.

8-Azaretene.—See A., 1942, II, 417.

Cyclisation of ureido-derivatives of unsymmetrical imino-dicarboxylic acids. Synthesis of hydantoins and related compounds. (Misses) D. R. Seeger and A. MacMillan (*J. Amer. Chem. Soc.*, 1942, **64**, 1686—1691).—*Me*$_2$ *phenylalanine*-N-*acetate* (**I**), b.p. 182°/10 mm. [hydrochloride (**II**) (modified prep.), m.p. 144—144·5° (gas)], with PhNCO in Et_2O gives *Me*$_2$ *phenylureidophenylalanine*-N-*acetate*, m.p. 124·5—125°, converted by NaOMe–EtOH and then HCl into *Me 3-phenyl-5-benzylhydantoin-1-acetate* (**III**), m.p. 159—160°. The corresponding hydantoin-*acid* (**IV**), +2H_2O (lost at 110°), m.p. 159·5—160° [with HCl–MeOH gives (**III**)], is obtained by treating CO_2H·CH_2·NH·CH(CH_2Ph)·CO_2H (**V**) with PhNCO or hydrolysing (**III**). Aq. KCNO and (**II**) give *Me*$_2$ *ureidophenylalanine*-N-*acetate*, m.p. 125—126° (and some Me 5-benzylhydantoin-1-acetate), which on hydrolysis is cyclised to yield 5-benzylhydantoin-1-acetic acid. 3-Phenyl-5-benzylidenehydantoin (**VI**), m.p. 252—252·5° (lit. 242—243°), with CH_2Cl·CO_2Et–NaOEt–EtOH gives *Et 3-phenyl-5-benzylidenehydantoin-1-acetate* (**VII**), m.p. 88·5—89°, converted by red P–HI at 140—145° into (**IV**) and thence (**III**) (proof of structure). 3-Phenyl-5-benzylidene-2-thiolhydantoin with the appropriate halogeno-ester and NaOEt–EtOH gives 86—96% of *Et 3-phenyl-5-benzylidenehydantoin-2-thiol-acetate*, m.p. 142—144°, *-phenylacetate*, m.p. 156—156·5°, and *-α-propionate*, m.p. 111—112°, all hydrolysed by boiling conc. HCl–EtOH to (**VI**). Br–AcOH converts (**VII**) into *Et 3-phenyl-5-α-bromobenzylidenehydantoin-1-acetate*, a-, m.p. 124—125°, and b-*forms*, m.p. 98—100°. RCOCl (1 mol.) and (**I**) (2 mols.) in Et_2O give *Me*$_2$ 3 : 5-*dinitrobenzoyl-*, m.p. 102—103°, and benzoylphenylalanine-*N*-acetate (**VIII**), an oil. RCOCl–$NaHCO_3$–NaOH–H_2O converts (**V**) into benzoyl- {*Na*$_2$, +2H_2O (retained at 110°), *forms*, m.p. 288—289° (decomp.) [also obtained from (**VIII**) by NaOH–aq. EtOH] and 272—273° (decomp.)} and m-*nitrobenzoylphenylalanine*-N-*acetic acid*, +2H_2O, *forms*, m.p. 90—92° (decomp. at 105°) and 130—131° (decomp.). R. S. C.

Heterocyclic compounds containing nitrogen. L. Reactions of β-ketoadipic ester; synthesis of heterocyclic compounds containing nitrogen, in particular, pyrrolones and *dl*-ecgonic acid. P. Ruggli and A. Maeder (*Helv. Chim. Acta*, 1942, **25**, 936—964).—Gradual addition of CO_2Me·$[CH_2]_2$·COCl in Et_2O to a suspension of CHAcNa·CO_2Et in Et_2O gives *Me Et β-keto-α-acetyladipate* (**I**), b.p. 129—131°/0·1—0·15 mm. (*Cu*, m.p. 85°, *Ni*, m.p. 112°, *Pd*^{II}, m.p. 138°, *Hg*^{II}, and *Co*, m.p. 94°, derivatives), and *Et β-β'-carbomethoxypropionoxycrotonate* (**II**), b.p. 162—164°/12 mm., which does not give a colour with $FeCl_3$. (**I**) and (**II**) can be separated since (**I**) is sol. and (**II**) insol. in saturated aq. Na_2CO_3. (**II**) is isomerised to (**I**) by K_2CO_3 and CH_2Ac·CO_2Et in boiling EtOAc. (**I**) is transformed by NHPh·NH_2 in 50% AcOH at room temp. into *Me 4-carbethoxy-1-phenyl-3(5)-methylpyrazole-5(3)-propionate*, b.p. 141—143°/0·008 mm., and by K_2CO_3 and NH_2·CO·NH·NH_2,HCl in aq. EtOH into *Me 1-carbamyl-4-carbethoxy-3(5)-methylpyrazole-5(3)-propionate*, m.p. 94°, converted by boiling H_2O into *Me 4-carbethoxy-3(5)-methylpyrazole-5(3)-propionate*, m.p. (+1H_2O), 57—58° (anhyd.) 79—80°. (**I**) and N_2H_4,H_2O at 0° and then in EtOH at 100° afford *4-carbohydrazido-3(5)-methylpyrazole-5(3)-propionhydrazide* (+1H_2O), softens at 133°, m.p. 140° (decomp.) (*dianisylidene* derivative, m.p. 219—220°). The first product of the action of cold NH_3 on (**I**) is a cryst. enol NH_4 salt, which is characterised as a derivative of the initial material by its ready conversion into the Cu compound. After 3 hr. with a defined excess of NH_3 at 25—30° the desired ammonolysis has occurred with production of NH_2Ac and *Me Et β-ketoadipate* (**III**), CO_2Me·$[CH_2]_2$·CO·CH_2·CO_2Et, b.p. 109°/0·015 mm., largely as the Et_2O-sol. *ketimide* (**IV**), which can be isolated as a liquid under defined conditions and certainly recognised as a first fission product of normal operation. It is converted into (**III**) by repeated treatment with HCl, the purity of (**III**) being checked by the rapidity with which it forms a Cu derivative. Unless (**IV**) is decomposed completely before distillation the product contains the *substance*, CO_2Me·$[CH_2]_2$·C(CH_2·CO_2Et):N·CO·CH_2·CO·$[CH_2]_2$·CO_2Me, m.p. 50—52°, characterised as the *Cu* compound, m.p. 185—186° (decomp.), and the *semicarbazone*, softens at ~128°, m.p. 131°. (**III**) is converted by NH_3–EtOH at 10—15° and then at 70° mainly into *Et pyrrol-5-one-2-acetate* (**V**), m.p. 82—83°, accompanied by some (**IV**). Prolonged contact with NH_3–H_2O–EtOH at room temp. transforms (**III**) or (**IV**) into *pyrrol-5-one-2-acetamide*, incipient decomp. 200°, m.p. 215—216°. Hot aq. alkali decomposes (**V**) completely with evolution of NH_3. Mild treatment with KOH–MeOH transforms (**V**) into the *K* salt of *Et 5-hydroxypyrrolenine-2-acetate*, softens slightly at 121°, m.p. 129—130°, also obtained from (**V**) and 2% aq. NaOH and re-converted into (**V**) by hot CCl_4. More protracted hydrolysis appears to transform CO_2Et into CO_2H but the ring is easily opened with evolution of NH_3 unless particular care is exercised. (**III**) and NH_2Me in EtOH at 0° yield *Et 1-methylpyrrol-5-one-2-acetate* (**VI**), m.p. 121—122°, or give *1-methylpyrrol-5-one-2-acetmethylamide*, m.p. 199°, if NH_2Me is used in large excess. With NH_2Et in EtOH at 0° (**III**) affords *Me Et β-ethyliminoadipate*, b.p. 120—122°/0·1 mm., transformed by conc. NH_3 in aq. EtOH into *Et 1-ethylpyrrol-5-one-2-acetate*, m.p. 48° or m.p. 50° after resolidification. *Me Et β-benzyliminoadipate*, b.p. 138—140°/0·015 mm., obtained similarly, is similarly transformed into *Et 1-benzylpyrrol-5-one-2-acetate*, m.p. 79°. (**III**) is transformed by NH_2Pr^{α} in EtOH at 0° followed by a large excess of conc. aq. NH_3 into *Et 1-n-propylpyrrol-5-one-2-acetate*, m.p. 45—46°, whilst very protracted interaction of (**III**) and NH_2Ph leads to *Et 1-phenylpyrrol-5-one-2-acetate*, m.p. 139—140°. *dl*-Ecgonic acid, m.p. 92—94°, is obtained by hydrogenating (**VI**) in EtOH–AcOH containing $FeCl_3$ and PtO_2 and hydrolysing the product. Gradual addition of NHPh·NH_2 in 50% AcOH to cold (**III**) in EtOH gives *Me 1-phenylpyrazol-5-one-3-propionate*, m.p. 79·5°, converted by NH_3 in aq. EtOH into the corresponding *amide*, m.p. 172° (decomp.). *Me Et β-ketoadipate-semicarbazone*, m.p. 89°, obtained by short action of NH_2·CO·NH·NH_2,HCl and K_2CO_3 in (**III**) in aq. EtOH, is transformed by conc. aq. NH_3 at room temp. and subsequently at 35° into *Me 1-carbamylpyrazol-5-one-3-propionate* (**VII**), m.p. 172—173°, brisk decomp. 195°, and by boiling EtOH into *Et 6-keto-1-carbamyltetrahydropyridazine-3-acetate*, softens at ~155°, m.p. 167°. N_2H_4,H_2SO_4, Na_2CO_3, and (**III**) in boiling EtOH afford *Me pyrazol-5-one-3-propionate*, softens slightly at 162°, m.p. 168°, whilst (**III**) and N_2H_4,H_2O at 0° give *pyrazol-5-one-3-propionhydrazide*, softens at ~130°, m.p. 178—179° (partial decomp.). (**III**) is semi-hydrolysed by KOH–MeOH and then transformed by NH_2·CO·NH·NH_2 into *1-carbamylpyrazol-5-one-3-propionic acid*, decomp. 195°, also obtained by hydrolysing (**VII**) by NaOEt in abs. EtOH at 100°. Boiling KOH–abs. MeOH converts (**VII**) into *pyrazol-3-one-3-propionic acid*, darkens at ~214°, m.p. 222—223° (decomp.). H. W.

Structural-chemical investigations. VII. Reactive behaviour of thiocarbamide towards unsaturated acids. H. Erlenmeyer and F. Heitz (*Helv. Chim. Acta*, 1942, **25**, 832—836).—Maleic, fumaric, and citraconic acid react with $CS(NH_2)_2$ with production of a thiazole ring, whereas a pyrimidine compound results from CHPh:CH·CO_2H (**I**) and CHMe:CPh·CO_2H (**II**). $CS(NH_2)_2$ and (**I**) at 240° afford 6-keto-2-thion-4-phenylhexahydropyrimidine, m.p. 240°, converted by aq. Pb(OAc)$_2$ into the 2 : 6-diketo-compound, m.p. 115°, not identical with *4-keto-2-imino-5-benzylthiazolidine*, m.p. 218°,

obtained by condensation of $CS(NH_2)_2$ and $CH_2Ph{\cdot}CHBr{\cdot}CO_2H$ at 135—140°, or by hydrogenation of 4-keto-2-imino-5-benzylidenethiazolidine, m.p. 280°, derived from $CS(NH_2)_2$ and $CHPh{:}CBr{\cdot}CO_2H$. Similarly $CS(NH_2)_2$ and (**II**) afford *6-keto-2-thion-5-phenyl-4-methylhexahydropyrimidine*, m.p. 221°, desulphurised by $Pb(OAc)_2$.

H. W.

5-Keto-2-thion-4-carbethoxy-I : 3-dihydropyrimidine and related compounds. J. H. Yoe and G. R. Boyd, jun. (*J. Amer. Chem. Soc.*, 1942, **64**, 1511—1513).—Et 5-keto-2-thion-1 : 3-dihydropyrimidine-4-carboxylate (**I**), m.p. 275° (purple colour with $AgNO_3$), is obtained from $NH_2{\cdot}CH_2{\cdot}CO_2Et$ by CS_2 in boiling 99% EtOH, but in 100% EtOH gives a compound, m.p. 181° (red colour with $AgNO_3$) (cf. Sheppard *et al.*, A., 1936, 1000). 5-Keto-2-thion-, decomp. ~150° (unstable white Ag derivative), and 2 : 5-diketo-1 : 3-dihydropyrimidine (white Ag derivative) are prepared from $CO(CH_2{\cdot}NH_2)_2$ (*dihydrochloride*) by CS_2 and $ClCO_2Et$, respectively; 2-thiol-4-thiocarbamido-, m.p. 212° (decomp.), and -4-amino-methyl-1 : 3-dihydropyrimidine, darkens at 240°, m.p. >350°, are prepared by KCNS. Only (**I**) is a sensitive reagent for $Ag^{\cdot}$.

R. S. C.

Piperazinium di-2-methyl-5-*iso*propylbenzenesulphonate. C. T. Bahner and D. Hamilton (*J. Amer. Chem. Soc.*, 1942, **64**, 1741).—This *salt*, m.p. >300°, is obtained by double decomp.

R. S. C.

Attempted synthesis of vinylneoxanthobilirubic acid. H. Lichtenwald (*Z. physiol. Chem.*, 1942, **273**, 118—127).—5-Carbethoxy-3-acetyl-2 : 4-dimethylpyrrole (cf. Fischer *et al.*, A., 1935, 632) and SO_2Cl_2–$CHCl_3$, followed by decomp. of the Cl_2-compound with H_2O, yield 5-carbethoxy-2-aldehydo-3-acetyl-4-methylpyrrole, and thence ($AgNO_3$–aq. EtOH–KOH) *5-carbethoxy-3-acetyl-4-methylpyrrole-2-carboxylic acid*, m.p. 142°, and (aq. NaOH) *4-acetyl-3-methylpyrrole-2 : 5-dicarboxylic acid*, m.p. 229° (decomp.), and (aq. NaOH at 160° in autoclave) 4-acetyl-3-methylpyrrole (**I**) (*ketazine*, $C_{14}H_{18}N_4$, m.p. 128·5°; *semicarbazone*, m.p. 195°; *4-acetyl-3-methylpyrrole-2-azobenzene*, m.p. 128·5°; $Et_2C_2O_4$–EtOH–Na give *Et 3-methyl-4-β-pyrroloylpyruvate*, $C_{11}H_{13}O_4N$, m.p. 179°). (**I**) and 5-bromo-2-aldehydo-3-methylpyrrole-4-propionic acid, with 48% HBr in MeOH at room temp., give *5′-bromo-4-acetyl-3 : 3′-dimethylpyrromethene-4′-propionic acid hydrobromide*, $C_{15}H_{18}O_3N_2Br$. (**I**), cryptopyrrolecarboxylic acid aldehyde, and HBr–MeOH (water-bath) afford *di-(carbomethoxy)cryptopyrrylmethene hydrobromide*, m.p. 211° (decomp.). 2-Aldehydo-4-acetyl-3-methylpyrrole and 2 : 4-dimethylpyrrole-3-propionic acid afford (HBr–MeOH) *Me 4-acetyl-3 : 3′ : 5′-trimethylpyrromethene-4′-propionate hydrobromide*, m.p. 191°. 5-Bromo-2-aldehydo-3-methyl-4-ethylpyrrole and 3-acetyl-2 : 4-dimethylpyrrole (HBr–EtOH) give *5-bromo-4′-acetyl-3 : 3′ : 5′-trimethyl-4-ethylpyrromethene hydrobromide* (darkens at 200°, does not melt at 300°), converted by KOAc–AcOH into *5-hydroxy-4′-acetyl-3 : 3′ : 5′-trimethyl-4-ethylpyrromethene*, m.p. 286°. The corresponding *oxime*, decomp. 273°, is hydrogenated (Raney Ni in EtOH at 140°/80 atm.) to *5-hydroxy-3 : 3′ : 5′-trimethyl-4 : 4′-diethylpyrromethane*, m.p. 161°. 3-Methylpyrrole and 5-aldehydo-2 : 4-dimethylpyrrole-3-propionic acid with 48% HBr–MeOH at 0° yield *3 : 3′ : 5′-trimethylpyrromethene-4′-propionic acid hydrobromide*, m.p. 223—225°. *3 : 4′-Diacetyl-3′ : 4 : 5′-trimethylpyrromethane-5-carboxylic acid*, m.p. 186°, is obtained by hydrolysis (aq. KOH–EtOH) of the corresponding Et ester (*loc. cit.*).

A. T. P.

Benziminazole rule for determining configuration of aldonic acids etc.—See A., 1942, II, 393.

1 : 9-Pyrazolanthrone-6-carboxylic acid.—See B., 1942, II, 363.

Naphtho*iso*triazine group. XIII. Taste and chemical constitution. A. Neri (*Gazzetta*, 1941, **71**, 201—208).—2 : 1 : 4-$PhN_2{\cdot}C_{10}H_5(NH_2){\cdot}SO_3Na$ with $Pr^{\alpha}CHO$, 3 : 4 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CHO$, $CHPhMe{\cdot}CHO$, $CH_2Ph{\cdot}CH_2{\cdot}CHO$, or *iso*-$C_5H_{11}{\cdot}C(:CHPh){\cdot}CHO$ in boiling AcOH gives respectively *3-phenyl-2-n-propyl-* (**I**), *-2-(3′-hydroxy-4′-methoxyphenyl)-* (**II**), *-2-α-* (**III**) and *-2-β-phenylethyl-* (**IV**), and *-2-α-isoamylstyryl-2 : 3-dihydro-1 : 3 : 4-naphthoisotriazine-6-sulphonic acid* (**V**). (**I**) and (**II**) are slightly bitter, (**III**) is bitter, (**IV**) has a sweet after-taste, and (**V**) is tasteless. The influences of the nature and position of substituents on the taste of compounds in this group are discussed.

E. W. W.

Semicarbazones and thiosemicarbazones of α-ketonic acids; tautomeric 5-hydroxy- and 5-keto-4 : 5-dihydro-derivatives of 1 : 2 : 4-triazoles. M. Girard (*Ann. Chim.*, 1941, [x], **76**, 326—394; cf. A., 1938, II, 284).—*p*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}C(CO_2H){:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$ (**I**) yields 3 : 5-diketo-6-*p*-methoxybenzyl-2 : 3 : 4 : 5-tetrahydro-1 : 2 : 4-triazine[3 : 5-dihydroxy-6-*p*-methoxybenzyl-1 : 2 : 4-triazine, *loc. cit.*] (**II**) [4-*N*-Me, m.p. 144°, 2 : 4-*NN*-Me_2, m.p. 89°, 4-*N*-Et, m.p. 140°, 2 : 4-*NN*-Et_2, m.p. 72°, 4-*N*-benzyl (**III**), m.p. 136°, and 2 : 4-*NN*-dibenzyl ether, m.p. 71°], converted (in H_2O) by Na–Hg into the acid *semicarbazide*, *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, m.p. 202°, and thence (I–KI–aq. Na_2CO_3) *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$. (**III**) and Na–Hg give the *benzylsemicarbazide*, *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CH_2Ph$, m.p. 172°, and thence (Nessler) the corresponding *benzylsemicarbazone*, m.p. 104°, and (I–KI–aq. Na_2CO_3) the *benzylsemicarbazone*, m.p. 119°, of p-*methoxyphenylacetaldehyde*. (**II**) and aq. NaOBr afford *αα-dibromo-β-p-methoxyphenylpropionamide*, m.p. 120°, converted by Zn–AcOH into *p*-$OMe{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}CO{\cdot}NH_2$. (**I**) and aq. Na_2CO_3–I–KI yield, through their K salts, stereoisomeric *α-iodo-p-methoxycinnamic acids*, m.p. 148—149° (stable form) and 112—113° (labile form, partly converted into the stable form by heating with aq. AcOH–HCl in a sealed tube at 100°), reduced by Zn–AcOH to *p*-$OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$. 5-Hydroxy-3-thiol-6-*p*-methoxybenzyl-1 : 2 : 4-triazine (*loc. cit.*) [5-keto-3-thiol-6-*p*-methoxybenzyl-4 : 5-dihydro-1 : 2 : 4-triazine] affords the *S*-Me, m.p. 211°, -Et, m.p. 187°, and -benzyl ether, m.p. 184° (Na–Hg yields *5-keto-3-benzylthiol-6-p-methoxybenzyl-1 : 2 : 5 : 6-tetrahydro-1 : 2 : 4-triazine*, m.p. 72°). The *NS*-$(CH_2Ph)_2$ ether and HCl–EtOH afford the *2-N-benzyl ether*, m.p. 120°, of (**II**). The Na salt of (**I**) and aq. KI–I ($+Na_2CO_3$) yield *5-keto-3-p-methoxybenzyl-4 : 5-dihydro-1 : 2 : 4-triazole*, m.p. 173° (hydrochloride), hydrolysed by acid or alkali to *p*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$, or transformed by dil. NaOH into *5-hydroxy-3-p-methoxybenzyl-1 : 2 : 4-triazole*, m.p. 228° (block) (*Ag_2* salt; *Ac* derivative, m.p. 185°). Similarly prepared are 5-hydroxy-3-phenyl-1 : 2 : 4-triazole, *5-hydroxy-3-benzyl-*, m.p. 225° (*Ag_2* salt; Ac derivative, m.p. 169°), and *-3-β-phenylethyl-1 : 2 : 4-triazole*, m.p. 208° (*Ag_2* salt; Ac derivative, m.p. 167°) (from *5-keto-3-β-phenylethyl-4 : 5-dihydro-1 : 2 : 4-triazole*, m.p. 192°).

A. T. P.

Associating effect of the hydrogen atom. Constitution of benztriazoles.—See A., 1942, I, 366.

Demolition of 2-phenylnaphtho-1′ : 2′-4 : 5-triazole by oxidation. (Signa.) E. Ghigi and T. Pozzo-Balbi (*Gazzetta*, 1941, **71**, 228—234).—With quinoline and Cu, 2-phenyl-4-*o*-carboxyphenyltriazole-5-carboxylic acid, obtained from 2-phenylnaphtho-1′ : 2′ : 4 : 5-triazole and alkaline $KMnO_4$, gives *2 : 4-diphenyl-1 : 2 : 3-triazole*, m.p. 56—57°, which with HNO_3 (*d* 1·52) gives *tri-*, m.p. 238—239°, and *2′ : 4′ : 2″ : 4″-tetranitro-2 : 4-diphenyltriazole*, m.p. 178—179°. The last is reduced (Fe, AcOH, HCl) to the $(NH_2)_4$-compound, m.p. ($+H_2O$) 132—135° (resolidifying and remelting at 182°), which with alkaline $KMnO_4$ gives 1 : 2 : 3-triazole-4-carboxylic acid, convertible into 1 : 2 : 3-triazole.

E. W. W.

Effect of light on riboflavin solutions.—See A., 1942, III, 909.

***iso*Oxazoles.**—See B., 1942, II, 363.

β-Alkylaminoethanols.—See A., 1942, II, 394.

***N*-Arylmorpholones.**—See B., 1942, II, 396.

Structure-chemical investigations. VIII. Thiazole-4 : 5-dicarboxylic acid and -4-carboxylic acid. H. Erlenmeyer and C. J. Morel (*Helv. Chim. Acta*, 1942, **25**, 1073—1077; cf. A., 1937, II, 241).—Et 2-aminothiazole-4-carboxylate, m.p. 172°, is diazotised in presence of H_3PO_4 (*d* 1·7) and HNO_3 (*d* 1·4) at −5° to 0° and then converted by Cu in presence of HBr (48%) into *Et 2-bromothiazole-4-carboxylate*, b.p. 152—154°/13 mm., m.p. 69—70°. This is hydrolysed and then dehalogenated in presence of Raney Ni to *thiazole-4-carboxylic acid*, m.p. 196—197° (corr.), identical with the product obtained by partial decarboxylation of thiazole-4 : 5-dicarboxylic acid and regarded (*loc. cit.*) as the -5-carboxylic acid.

H. W.

2-*N′*-Sulphanilamido-4-*n*-propylthiazole. K. Ganapathi, M. V. Shirsat, and C. V. Deliwala (*Current Sci.*, 1942, **11**, 103—104; cf. A., 1942, II, 208).—$Pr^{\alpha}COCl$ and CH_2N_2 give $COPr^{\alpha}{\cdot}CHN_2$ and thence (HCl–Et_2O) $COPr^{\alpha}{\cdot}CH_2Cl$, which with $CO(NH_2)_2$ yields 2-amino-4-*n*-propylthiazole (picrate, m.p. 192°), converted into *2-N′-sulphanilamido-4-n-propylthiazole*, m.p. 143—144° (*Ac* derivative, m.p. 202°).

A. T. P.

Dicarboxylic acid derivatives of sulphonamides. M. L. Moore and C. S. Miller (*J. Amer. Chem. Soc.*, 1942, **64**, 1572—1576).—$(CH_2{\cdot}CO)_2O$, $(CH{\cdot}CO)_2O$, or *o*-$C_6H_4(CO)_2O$ (1·25 mol.) with the appropriate sulphanilamide in boiling EtOH or dioxan gives (usually <80%) *2-N⁴-β-carboxypropionylsulphanilamido-pyridine*, decomp. 135—140° (191—194° after 7 months; lit. 145°), *-thiazole* (**I**), decomp. 192—195° (unstable *form*, decomp. 184—186°), *-5-ethyl-4-thiazolone*, decomp. 161—162°, *-5 : 5-diethyl-4-thiazolone*, decomp. 208—209°, *-guanidine*, decomp. 214—215°, *-pyrimidine*, decomp. 212—213°, and *-4-methylpyrimidine*, decomp. 201—202°, resolidifies, remelts at 270°, *N⁴-β-carboxypropionylsulphon-p-sulphamylanilide*, decomp. 234°, and *-p-2′-thiazolylsulphamylanilide*, decomp. 237°; *2-N⁴-β-carboxyacrylylsulphanilamido-pyridine*, decomp. 193—194° (lit. 208°), *-thiazole*, unstable in solution, decomp. 215—216°, *-5-ethyl-4-thiazolone*, decomp. 179—181°, and *-guanidine*, decomp. 201—202°, *2-N⁴-o-carboxybenzoylsulphanilamido-thiazole*, decomp. ~260°, and *-guanidine*, m.p. 266—267°. $Et_2C_2O_4$ or $CH_2(CO_2Et)_2$ (not Et_2 glutarate or sebacate) and the appropriate amine at 130—150° give, after hydrolysis (2·5% NaOH at 85—95°) (usually ~80%), *2-N⁴-H oxalylsulphanilamido-thiazole*, hygroscopic, decomp. 207—208° (*Et* ester, decomp. 233—234°), and *-pyrimidine*, decomp. ~250° (*Et* ester, decomp. 230—235°), *2-N⁴-carboxyacetylsulphanilamido-thiazole*, decomp. ~240—250° (*Et* ester, decomp. 193—194·5°), *-guanidine*, decomp. 172—175° (loses CO_2 to give the N^4-Ac compound) (*Et* ester, decomp. 225—226°), and *-pyrimidine*, m.p. 215—216° (*Et* ester, m.p. 198—199°). $(CH_2{\cdot}CO_2H)_2$ (**II**) (1) and

sulphathiazole (**III**) (1 mol.) at 150—160° give 2-p-*succinimidobenzenesulphonamidothiazole* (**IV**), m.p. 266—267° [hydrolysed by boiling 5% NaOH to (**I**)], and a little 2 : 2′-N⁴N⁴′-*succindi(sulphanilamidothiazole)* (**V**), m.p. 277—279° (decomp.), or, after treatment of the crude product with aq. NH_3, a *product*, m.p. 194·5—195·5°, hydrolysed to (**I**) by 5% NaOH at 90°. (**II**) (0·411) and (**III**) (0·392 mol.) alone at ~165° or in $(OEt·[CH_2]_2)_2O$ give, after treatment with 10% NaOH, (**I**) and a little (**V**). $CO_2H·[CH_2]_8·CO_2H$ and (**III**) at 150—170° give, after treatment with 10% NaOH, 2 : 2′-N⁴N⁴′-*sebacdi(sulphanilamidothiazole)*, m.p. 245—246°, and 2-N⁴-*θ-carboxy*-n-*nonoylsulphanilamidothiazole*, m.p. 171—172°. N⁴N⁴′-*Adipdi(sulphanilamidoguanidine)*, m.p. 268—269° (decomp.), 2-N⁴-*δ-carboxy*-n-*valerylsulphanilamido-pyridine* (11%), m.p. 184—185°, *-thiazole* (47%), m.p. 196—197°, and *-pyrimidine*, decomp. 188°, N⁴-*δ-carboxy*-n-*valerylsulphanilamidoguanidine* (18%), m.p. 132—133°, 2 : 2′-N⁴N⁴′-*glutardi(sulphanilamidothiazole)*, m.p. 251—254° (decomp.), and 2-N⁴-*γ-carboxy*-n-*butyrylsulphanilamidothiazole*, decomp. 196—197°, are similarly prepared. *p*-$(CH_2·CO)_2N·C_6H_4·SO_2Cl$, m.p. 189—195° (decomp.) (cf. lit.) (1 mol.), with 2-aminothiazole (**VI**) (2 mols.) in C_5H_5N or $COMe_2$ or with 1 mol. of (**VI**) and Na_2CO_3 gives (**I**) and a product, m.p. 250·5—251·5° (decomp.). R. S. C.

Thiazoles.—See B., 1942, II, 397.

Naphthoselenazoles.—See B., 1942, II, 364.

Polymethine dye intermediates.—See B., 1942, II, 363, 366.

Carbocyanines.—See B., 1942, II, 363.

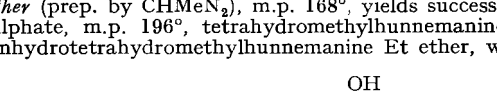
Acenaphthene series. I. Mono- and di-*tert.*-butyl-acenaphthene, -acenaphthenequinone, and -naphthalic anhydride, and their derivatives. A. T. Peters (*J.C.S.*, 1942, 562—565).—Acenaphthene and Bu^tCl–$AlCl_3$–CS_2 give 3-tert.-*butyl-* (**I**), m.p. 73—74°, b.p. 170—174°/7 mm. (*picrate*, m.p. 86—90°), and 3 : 4-di*tert.-butyl-acenaphthene* (**II**), m.p. 162—163° (*picrate*, m.p. 104°). (**I**) is oxidised by boiling $Na_2Cr_2O_7$–AcOH to 4-tert.-*butylnaphthalic anhydride*, m.p. 201—202° (*imide*, m.p. 256°; N-*methylimide*, m.p. 173°; *phenylhydrazide*, m.p. 187—188°), converted by *o*-$C_6H_4(NH_2)_2$–AcOH into 9′-*keto*-3′- (or 4′-)tert.-*butyl*-8′-*azaphenalino*-(7′ : 8′ : 2 : 3)-*ψ-indole*, m.p. 194—195°. Controlled oxidation of (**I**) with $Na_2Cr_2O_7$–AcOH at 105° yields 3-tert.-*butylacenaphthenequinone*, m.p. ~156—159°, converted by 2-hydroxythionaphthen in AcOH–HCl into 3′-tert.-*butyl*-1 : 7′-*thionaphthenacenaphthenylindigo*, m.p. 300—301°. (**II**) gives 4 : 5-di*tert.-butylnaphthalic anhydride* (**III**), m.p. 211° (*imide*, m.p. 240°; N-*methylimide*, m.p. 231—232°; *phenylhydrazide*, m.p. 180°; 9′-*keto*-3′ : 4′-di*tert.-butyl*-8′-*azaphenalino*-(7′ : 8′ : 2 : 3)-*ψ-indole*, m.p. 278—279°). Controlled oxidation of (**II**) yields a double *compound*, m.p. 186°, of (**III**) and 3 : 4-di*tert.-butylacenaphthenequinone*, the latter, m.p. 213—214° (*diphenylhydrazone*, m.p. 240—242°; p-*nitrophenylhydrazone*, m.p. 285—287°; 2 : 4-*dinitrophenylhydrazone*, m.p. 324°; *bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 320°), being obtained pure by repeated extraction with 10% aq. Na_2CO_3 at 170°. The derived 3′ : 4′-di*tert.-butyl*-1 : 7′-*thionaphthenacenaphthenylindigo*, m.p. 260—262°, and its 5-*OEt*-derivative, m.p. 262—265°, are vat dyes. A. T. P.

VII.—ALKALOIDS.

***Sophora* alkaloids. III. Alkaloids of the seeds of *S. chrysophylla*.** L. H. Briggs and W. E. Russell (*J.C.S.*, 1942, 507—509).—Seeds of *S. chrysophylla* yield 2% of crude alkaloids, containing anagyrine (4 pts.), cytisine (1 pt.), and a small amount of *sophochrysine*, $C_{13-15}H_{21-19}O_2N_3$, m.p. 284—287°, $[\alpha]_D^{25}$ −113·2° in alcohol [*picrate*, darkens at 250°, m.p. >360°; *picrolonate*, m.p. 265·5—267° (decomp.); aurichloride, m.p. 190—192° (decomp.)], identical with base *D* from *S. microphylla* and *S. tetraptera* (A., 1938, II, 35, 422). R. S. C.

***Sophora* alkaloids from seeds of Chatham Islands species.**—See A., 1942, III, 863.

Alkaloids of papaveraceous plants. XXXIV. *Hunnemannia fumariaefolia*, Sweet. Constitution of a new alkaloid, hunnemanine. R. H. F. Manske, L. Marion, and A. E. Ledingham (*J. Amer. Chem. Soc.*, 1942, **64**, 1659—1661; cf. A., 1942, II, 275).—This plant yields protopine, *allo*cryptopine (**I**), a non-phenolic *alkaloid* [*F* 58], $C_{20}H_{15}O_3N(OMe)_2$, m.p. 174°, and *hunnemanine* (**II**), m.p. 209°. (**II**) has the structure shown, since with CH_2N_2–Et_2O it gives (**I**), and its *Et ether* (prep. by $CHMeN_2$), m.p. 168°, yields successively the methosulphate, m.p. 196°, tetrahydromethylhunnemanine Et ether, and anhydrotetrahydromethylhunnemanine Et ether, which

(II.) 

with $KMnO_4$ in $COMe_2$ at 3° gives 4-*methoxy*-3-*ethoxy*-2-*methylbenzoic acid* (**III**), m.p. 175°. 2 : 3 : 1-$OEt·C_6H_3(OMe)·CHO$ with Zn–Hg–HCl–PhMe gives 3-*methoxy*-2-*ethoxytoluene*, b.p. 72—74°/4 mm., converted by HCl–HCN–$AlCl_3$–C_6H_6 into 4-*methoxy*-3-*ethoxy*-2-*methylbenzaldehyde*, m.p. 24°, b.p. 121—123°/3 mm. (*oxime*, m.p. 88°), and thence ($KMnO_4$) (**III**) (m.p. 177°). R. S. C.

VIII.—ORGANO-METALLIC COMPOUNDS.

Phosphonitrilic compounds. I. Phenyl derivatives of triphosphonitrilic chloride. H. Bode and H. Bach (*Ber.*, 1942, **75**, [*B*], 215—226; cf. Schenck and Römer, A., 1924, ii, 752).—Contrary to Rosset (A., 1925, I, 600) triphosphonitrilic chloride (**I**) could not be caused to react with MgPhBr; with LiPh it gives a small yield of a product (not isolated) hydrolysed to $OH·PPh_2{:}O$. With $AlCl_3$ in CS_2 (**I**) gives the *compound*, $P_3N_3Cl_6,2AlCl_3$. (**I**), $AlCl_3$ (2 mols.), and C_6H_6 yield *tetrachlorodiphenylphosphonitrile*, $N_3P_3Cl_4Ph_2$ (**II**), m.p. 92·5; Cl is not further displaced by use of a greatly increased proportion of $AlCl_3$ and introduction of further Ph groups cannot be effected by the action of $AlCl_3$ on (**II**). H_2O at 150—160° hydrolyses (**II**) to $OH·PPh_2{:}O$, showing that 2 Ph and therefore probably 2 Cl are attached to P. At 250° (**II**) becomes polymerised to a solid white mass. Treatment of (**II**) with MgPhBr in PhMe gives an impure product, m.p. 185—187°, transformed by $AgClO_4$ in EtOH into the *perchlorate*, $N_3P_3Ph_7H,HClO_4$, m.p. 181°, in which the seventh Ph is also attached to P since hydrolysis leads to the formation of PPh_3O in large amount. If PhMe is replaced by PhOMe hexaphenyltriphosphonitrile, m.p. 228°, is obtained in small proportion; this is hydrolysed exclusively to $OH·PPh_2{:}O$, showing that all 6 Ph and hence all 6 Cl are attached in pairs to P. $PPhCl_2$ in $C_2H_2Cl_4$ is transformed by Cl_2 into $PPhCl_4$, which with NH_4Cl at 140° gives *chlorodihydroxytriphenyltriphosphonitrile*, $N_3P_3Ph_3Cl(OH)_2$, m.p. 294°, hydrolysed by EtOH–conc. HCl at 150° to $PPhO(OH)_2$. H. W.

Potassium alkaneselenonates and other alkyl derivatives of selenium. (Miss) M. L. Bird and F. Challenger (*J.C.S.*, 1942, 570—574).—Oxidation ($KMnO_4$) of the appropriate seleninic acids gives *K methane-*, *ethane-*, and *propane*-1-*selenonate*, which with hot dil. acid eliminate H_2SeO_3, and Me_2Se is similarly oxidised to $MeSeO_3H$. *Dimethylselenetine bromide*, $Me_2SeBr·CH_2·CO_2Et$, has m.p. ~90° (decomp.), Et_2SeBr_2 has m.p. 37° (decomp.), and the Pr^a_2 compound, m.p. 50°, the two latter substances being oxidised (Ag_2O–H_2O) to alkaneseleninic acids. Oxidation (H_2O_2) of Me_2Se affords $MeSeO_2H$, which with HBr yields *methylselenium tribromide*, m.p. 75° (decomp.), since the acid is mixed with $Me_2Se(OH)_2$ or Me_2SeO. Dialkyl diselenides can be converted into Me alkyl selenides by reduction (Na–EtOH) and treatment with MeI and they undergo fission with Hg^{II} salts. *Me Et selenide dimercurichloride* has m.p. 141·5° (decomp.), *Me Pr^a selenide mercurichloride*, m.p. 88°, and the Pr^a_2 compound, m.p. 93—94°. F. R. S.

Syntheses involving utilisation of magnesium allyl bromide in the Grignard reaction. H. R. Henze, B. B. Allen, and W. B. Leslie (*J. Org. Chem.*, 1942, **7**, 326—335).—The yields of products obtained from pre-formed Mg allyl bromide and typical saturated and unsaturated aldehydes and ketones, alkoxy-ketones, and esters exceed those obtained by simultaneous admixture of allyl halide, Mg, and reacting compound in dry Et_2O. The reagent is obtained by stirring Mg and C_3H_5Br (3 : 1 equivs.) in Et_2O (9 vols.) for 6—7 hr. at room temp. and then warming the mixture for 30 min. Unchanged metal is removed by use of a coarse filter, after which rather < 1 equiv. of the CO-compound dissolved in an equal vol. of dry Et_2O is added to the cooled reagent. The product is decomposed with ice and dil. HCl. The following are obtained in % yields placed in parentheses: $OH·CHEt·CH_2·CH{:}CH_2$, b.p. 131·5—120° (corr.)/753 mm., 56—58°/33 mm. (52), from EtCHO; $OH·CHPr^a·CH_2·CH{:}CH_2$, b.p. 151·7—152·2° (corr./743 mm., 61°/20 mm. (57), from Pr^aCHO; Δ^{α}-*octen-δ-ol*, b.p. 68—69°/10 mm. 171·5—172·0° (corr.)/748 mm. (65), from Bu^aCHO; $OH·CMe_2·CH_2·CH{:}CH_2$ b.p. 118—118·2° (corr.)/744·5 mm., 46·0—46·5°/30 mm. (53), from $COMe_2$; $OH·CMeEt·CH_2·CH{:}CH_2$, b.p. 138·0—138·5° (corr.)/742 mm., 60·5—61·0°/35 mm. (84), from COMeEt; $OH·CMeBu^{\beta}·CH_2·CH{:}CH$ (**I**), b.p. 76°/26 mm., 168·3—168·8° (corr.)/757·5 mm. (83), from $COMeBu^{\beta}$; $\Delta^{\alpha\epsilon}$-hexadien-γ-ol, b.p. 133·5—134° (corr.)/754 mm., 60·5—61·5°/40 mm. (66), from $CH_2{:}CH·CHO$; $\Delta^{\alpha\epsilon}$-heptadien-δ-ol, b.p. 62·0—62·5° (corr.)/15 mm., 155—156°/742 mm. (82), from $CHMe{:}CH·CHO$; δζ-dimethyl-$\Delta^{\alpha\epsilon}$-heptadien-δ-ol, b.p. 47—48°/4 mm., 72°/18 mm. (91), from mesityl oxide, reduced (PtO_2) to *ββδ-dimethylheptan-δ-ol*, b.p. 79°/26 mm., 171·3—171·8° (corr.)/756 mm., also obtained similarly from (**I**); *β-methoxy-γ-methyl-*Δ^{ϵ}*-hexen-γ-ol*, b.p. 166·0—166·5° (corr.)/737 mm. (70), from *Me α-methoxyethyl ketone*, b.p. 114·0—114·5° (corr.)/745 mm.; *δ-ethoxymethyl-*$\alpha^{\alpha\zeta}$*-heptadien-δ-ol*, b.p. 86—87°/15 mm., 198·0—198·5° (corr.)/744·3 mm. (90), from *Pr^a ethoxyacetate*, b.p. 173·5° (corr.)/748 mm.; δ-ethyl-$\Delta^{\alpha\zeta}$-heptadien-δ-ol, b.p. 82—84°/32 mm., 176·5—177·0° (corr.)/750 mm. (66), from $EtCO_2Et$. H. W.

Tin tri-*o*-tolyl and the instability of organo-metallic free radicals. H. Morris, W. Byerly, and P. W. Selwood (*J. Amer. Chem. Soc.*, 1942, **64**, 1727—1729).—By magnetic measurements *Sn tri*-o-*tolyl* (prep. described) is dimeric. Ebulliometric measurements on solu-

tions of $SnMe_3$ and $PbPh_3$ in C_8H_6 emphasise the unreliability of such methods for the study of free radicals since in both cases results indicate that decomp. of dimeride occurs readily.

W. R. A.

IX.—PROTEINS.

Colour test for tryptophan in protein hydrolysates.—See A., 1942, III, 864.

Structure of proteins.—See A., 1942, I, 386.

Progressive iodination of serum-albumin.—See A., 1942, III, 808.

Use of sulphur as reagent for determining thiol groups in ovalbumin.—See A., 1942, III, 864.

Copper-containing protein from cow's milk.—See A., 1942, III, 821.

X.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Chemistry of pongamol. I. S. Rangaswami and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **15, A**, 417—423; cf. A., 1942, II, 123).—Pongamol (**I**), $C_{18}H_{14}O_4$, m.p. 128—129° [p-*nitrobenzoate*, m.p. 200—205° (sinters at 105°)], contains 1 OH and 1 OMe, and is probably a flavone derivative. (**I**) and HBr or HI (*d* 1·7) in boiling Ac_2O give a non-phenolic *compound*, (?) $C_{17}H_{12}O_4$, m.p. 145—146°, whereas $AlCl_3$ in boiling C_6H_6 converts (**I**) into norpongamol, $C_{17}H_{12}O_4$, m.p. 224—225°. (**I**) and Br–AcOH at room temp afford a Br_4-derivative, $C_{18}H_{14}O_4Br_4$, sinters at 70° and decomp. >125°, which with boiling $COMe_2$ gives the *compound*, $C_{18}H_{13}O_4Br_3$, m.p. 83° (sinters at 65°; decomp. vigorously at 100°). (**I**) is oxidised by $KMnO_4$ to BzOH. A. T. P.

Isolation of cicutin from *Cicuta maculata*, L. L. Marion (*Canad. J. Res.*, 1942, **20, B**, 157—160).—Cryst. *cicutin*, $C_{19}H_{13}O_4(OMe)_3$, m.p. 171° (corr.) (from the light petroleum extract of the roots of *C. maculata*, L.), is unaffected by CH_2N_2, but with NaOH and Me_2SO_4 yields a *Me* derivative, m.p. 194—195° (corr.). Potentiometric titration shows that cicutin is a lactone. A. Li.

Chemical investigation of Indian fruits. III. Characteristic crystalline components of certain citrus fruits (oranges of the Circars). K. C. Patnayak, S. Rangaswami, and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **16, A**, 10—15; cf. A., 1941, II, 20).—The important citrus fruits (oranges) of the Northern Circars belong to three species, viz., *C. aurantium*, *C. medica*, and *C. decumana*, the sweet, sour, and bitter types, respectively. In the two former varieties, hesperidin is present, whereas naringin is the bitter principle of *C. decumana*. Extraction with ligroin of the peels of kamala (*C. aurantium*) gives *aurantin*, $C_{21}H_{22}O_8,H_2O$, sinters at 83°, m.p. 125—126°, which contains 6 OMe, and is of the type of tangeritin and nobiletin; it is demethylated by HI–PhOH at 140—150° (CO_2) to a *nor-aurantin* (? a flavanol), $C_{15}H_{10}O_8$, decomp. >320° [*hexa-acetate*, m.p. 238—240° (sinters slightly at 231°)]. A. T. P.

Chemistry of gossypol. I. Preparation and properties. V. K. Murty, K. S. Murty, and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1942, **16, A**, 54—61).—The disintegrated seeds of Cambodia cotton (*Gossypium hirsutum*) are extracted with $CHCl_3$, without previous addition of H_2O or removal of oil, the extracts are treated with NH_2Ph, and the NHPh-compound, m.p. 303° (decomp.), is decomposed by boiling Ac_2O, giving gossypol-acetic acid, m.p. 185° (decomp.). With boiling H_2O, this affords gossypol, $C_{30}H_{30}O_8$, m.p. 189° (decomp.); samples from all solvents had the same m.p. A. T. P.

Lignin. LI. Comparative oxidation of vanillin and lignin. H. Richtzenhain (*Ber.*, 1942, **75**, [*B*], 269—290).—Oxidation of HCl-lignin (**I**) by 20% H_2O_2 in presence of $BaCO_3$ for 20 hr at 90° gives an undissolved residue or non- or partly oxidised material of which ~30% is sol. in Na_2CO_3 and the remainder completely sol. in NaOH; it contains a small proportion of Ba salts including the oxalate and malonate. From the dissolved portion, apart from considerable amounts of HCO_2H and AcOH, it is possible to isolate 22% of the dissolved (**I**) as non-volatile acids of which only 13·1% can be converted into distillable esters by treatment with CH_2N_2. The remaining acids appear to be of high mol. wt. The following are isolated, the figures in parentheses being the % of the wt. of dissolved (**I**): $OH{\cdot}CH_2{\cdot}CO_2H$ (1·47), $OH{\cdot}CHMe{\cdot}CO_2H$ (0·21), $CH_2(CO_2H)_2$ (1·01), $(CH_2{\cdot}CO_2H)_2$ (1·83), $OH{\cdot}CH(CO_2H)_2$ (0·40) [*dibenzylidenehydrazide*, m.p. 224° (decomp.)], $CO_2H{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H$ (1·00), veratric (0·54), tricarballylic (0·26), β-hydroxyglutaric (0·21) (*dihydrazide*, m.p. 172°), $H_2C_2O_4$ (1·01), *acid* (**II**), $C_9H_8O_3N$, m.p. 188—189°, *iso*hemipinic (0·10), and 4-hydroxy-5-methoxy*iso*phthalic acid (0·04). Under like conditions vanillin affords only HCO_2H, AcOH, $H_2C_2O_4$, $OH{\cdot}CH_2{\cdot}CO_2H$, $CH_2(CO_2H)_2$, $(CH_2{\cdot}CO_2H)_2$, $OH{\cdot}CH(CO_2H)_2$, and $CO_2H{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H$. Acids of higher mol. wt. are present in small proportion but could not be obtained pure. Oxidations at 60° for 20 hr. and 10 hr. respectively give greatly increased yields of acids and other products, particularly a monohydroxy monomethoxy monobasic *acid*, $C_{11}H_3O_6$, m.p. 295° (decomp.) [*acetate*, m.p. 234° (decomp.); *Me* ester, m.p. 214°], (**II**), and small amounts of a *compound*, $C_9H_{12}O_5$, m.p. 143°, which contains at least 1 phenolic OH and 2 OMe. Ozonisation of (**I**) in EtOAc and treatment of the dissolved portion with H_2–Pd–$BaSO_4$ leads to a pale yellow amorphous ppt. in amount equal to ~30—40% of the (**I**) used. This substance very readily gives $H_2C_2O_4$ but a homogeneous cryst. or volatile product could not be obtained from it. Methyl-lignin gives an analogous product. H. W.

XI.—ANALYSIS.

Detection of elements in organic substances. L. Rosenthaler (*Pharm. Acta Helv.*, 1941, **16**, 189—192).—N is detected by heating with aq. KOH–$KMnO_4$ and passing the vapours into Nessler solution. Many N-free substances form volatile aldehydes but the ppt. produced in the Nessler solution is insol. in AcOH. The reaction is not quant.; part of the NH_3 is oxidised to HNO_2. With acid–$KMnO_4$ many N compounds form HNO_3; 0·01 g. is heated with H_2SO_4 (1 c.c.), cooled, diluted, and $KMnO_4$ added. The filtrate is decolorised with $H_2C_2O_4$ and treated with $NHPh_2$–H_2SO_4. E. H. S.

Determination of iodine with the apparatus of Grote and Krekeler or Wurzschmitt and Zimmermann.—See A., 1942, I, 407.

Microdiffusion methods. Ammonia and urea using buffered absorbents.—See A., 1942, III, 952.

Quantitative separation of amino-acids by exchange adsorption on aluminium oxide. T. Wieland (*Z. physiol. Chem.*, 1942, **273**, 24—30).—When neutral solutions of lysine and arginine hydrochloride are treated with Merck's Al_2O_3 the NH_2-acids are completely adsorbed, and can be eluted with water or PO_4''' buffer (p_H 7·0). Under the same conditions amino-dicarboxylic acids are not adsorbed, whilst histidine is only very slightly adsorbed. Al_2O_3 pretreated with dil. HCl adsorbs asparagine and glutamic acid but not neutral or basic NH_2-acids. Methods for the separation of basic from neutral, acid from neutral, and acid and basic from neutral NH_2-acids are described. J. N. A.

Necessary precaution in use of takadiastase for determination of maltose.—See A., 1942, III, 863.

Chemical and biological determination of choline.—See A., 1942, III, 952.

Applications of the bromometric assay. II. Bromination of derivatives of aminobenzenesulphonic acids.—See A., 1942, II, 400.

Photometric determination of tocopherol (vitamin-*E*). G. G. Villela (*Anais Assoc. Quim. Brasil*, 1942, **1**, 37—41).—α- and β-Tocopherol can be determined in presence of o-$C_6H_4(OH)_2$ by the method of Furter *et al.* (A., 1939, III, 404) if EtOH is replaced by $Bu^{\beta}OH$. F. R. G.

Effect of *p*-aminobenzoic acid on microbiological assay for nicotinic acid.—See A., 1942, III, 832.

Detection of organic compounds. L. Rosenthaler (*Pharm. Acta Helv.*, 1942, **17**, 100—109; cf. A., 1940, II, 240).—A new reagent for the detection of alkaloids is prepared by addition of just insufficient $Na_2S_2O_3$ to dissolve the solid in a suspension of CuI, followed by filtration of the mixture. It is not very sensitive, giving only a turbidity with a 0·1% solution of alypine or a 1·0% solution of tropacocaine, but more conc. solutions give typical cryst. complexes. An ammoniacal solution of $Tl(OAc)_3$ gives typical cryst. compounds with solutions of PhOH 2·5%, resorcinol 2%, pyrocatechol 1%, thymol 2%, quinol 2%, phloroglucinol 2%, orcinol 2%, o-$OH{\cdot}C_6H_4{\cdot}CO_2Na$ 5%, and morphine 2% in 2N-NaOH. α- and β-naphthol, pyrogallol, vanillin, and guaiacol give amorphous ppts. The Vitali reaction for cocaine is given by other compounds containing Bz, but not by those containing p-$NH_2{\cdot}C_6H_4{\cdot}CO$· (*e.g.*, novocaine). P. G. M.

Micro-determination of quinine.—See A., 1942, III, 864.